The Effect of Ultrasound for Fouling Mitigation in the Microfiltration of an Activated Sludge-Lagoon Effluent

Thesis submitted for the Degree of Master of Engineering

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Declaration

I hereby declare that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; and, any editorial work, paid or unpaid, carried out by a third party is acknowledged.

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Date_____

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List of Publications and Presentations

Publications

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Abbreviation

Symbol	Description
ACH	(poly)aluminium hydrate
ATR- FTIR	Attenuated total reflectance - Fourier transform infrared
BW	Backwashing
COD	Chemical oxidation demand
CIP	Cleaning-in-place
DBPs	Disinfection by-products
DOC	Dissolved organic carbon
EDTA	Ethylene diamine tetra acetic acid
EDX	Energy dispersive X-ray
EEM	Excitation emission matrix
EfOM	Effluent organic matter
EPS	Extracellular polymeric substances
IC	Inorganic carbon
LC-OCD	Liquid chromatography - organic carbon detection
MBRs	Membrane bioreactors
MF	Microfiltration
MW	Molecular weight
NOM	Natural organic matter
PACl	Polyaluminium chloride
PVDF	Polyvinylidene difluoride
SEM	Scanning electron microscopy
SMPs	Soluble microbial products
SUVA	Specific ultraviolet absorbance
TC	Total carbon
TMP	Transmembrane pressure
UF	Ultrafiltration
US	Ultrasound
UV	Ultraviolet
WWTP	Wastewater treatment plant

Summary

Low pressure membrane filtration such as microfiltration and ultrafiltration is playing an increasingly important role in the reclamation of municipal wastewater. However, membrane fouling remains a critical factor affecting the efficiency of the membranes in the filtration of the biologically treated secondary effluent.

Ultrasound (US) has traditionally been used for surface cleaning and dispersion purposes. Recent studies have demonstrated its potential for the control of membrane fouling and modification of the adsorption characteristics of organic substances. However, there is little information available on its application for the mitigation of fouling during wastewater treatment. Therefore, this study was aimed at investigating the potential of US for membrane cleaning and feed pre-treatment in the microfiltration of municipal activated sludge-lagoon effluent.

The polyvinylidene fluoride (PVDF) microfiltration (MF) membrane chosen for this study is often used in wastewater treatment. Ultrasound (45 kHz, 107 W) was used to clean membranes fouled with the wastewater effluent and its effectiveness was compared with that of backwashing in terms of the flux recovery and membrane surface analyses.

Application of US to the fouled membranes for greater than 5 min gave greater cleaning efficiency with flux recovery of over 80% compared with backwashing (74%). With a different water sample the flux recovery was similarly high (84%) after US, whereas it was only 56% after backwashing. The better performance of US was attributed to the cavitational shear forces induced by US which dislodged the cake layer and loosened the materials clogging the membrane pores. When US cleaning was followed by backwashing, flux recovery was enhanced further, this was attributed to the dislodged foulants being effectively flushed away from the membrane surface and pores by backwashing. However, flux recoveries decreased with successive fouling and cleaning cycles, the decrease being greater for backwashing (64% for US after 5 cycles, three times that for backwashing). These results were consistent with membrane analysis by attenuated total reflectance - Fourier transform infrared (ATR-FTIR) and scanning

electron microscopy (SEM). The increased irreversible fouling was due to compaction of the foulants and their increased affinity to the membrane surface and pores during the operation under pressure.

When used as feed pre-treatment, sonication led to some dissolution and fragmentation of the particulate matter in the effluent, these smaller particles had a negative impact on permeate flux by causing rapid blockage of the pores. However, sonication led to decreased irreversible fouling. Surface analysis (ATR-FTIR) of membranes fouled with sonicated effluent showed that US modified the characteristics of the effluent organic matter (EfOM) by altering the structure/conformation of proteins, which apparently reduced their potential to adsorb to the membranes.

US treatment followed by Al^{3+}-based coagulation using aluminium sulphate or polyaluminium chlorohydrate (ACH) achieved a greater increase in permeate flux compared with coagulation alone. This effect was greater at relatively higher turbidity (8.0 NTU) compared with lower turbidity (i.e., 1.0 and 3.6 NTU). This increase was due, at least in part, to the breakdown of the particles to form more nuclei for coagulation. Furthermore, the physico-chemically modified EfOM may have enhanced interaction with the hydrolysed Al species, which led to the formation of a cake layer with less filtration resistance. These changes influenced the size of the coagulation flocs, increasing the diameter by approximately 20–30%. Flux recovery was greater when US was used before ACH, and decreased only slightly with successive fouling and cleaning cycles. The enhanced cleaning performance may be due to the lower affinity of ACH flocs for the membrane materials. As alum treatment alone achieved good flux recovery, there was not a significant benefit from employing US for mitigating irreversible fouling.

This work demonstrated the potential of US for mitigating membrane fouling. However, the integration of the US transducers within the membrane system will be a major challenge for the application of US in membrane cleaning. It is more appropriate that US is used as pre-treatment to the membrane system, the transducers can be placed prior to the coagulant feed line. Further work on the determination of the detailed

mechanisms associated with enhancing coagulation would enable optimisation of the system with regard to process, cost and energy efficiency.

Chapter 1. Introduction

Wastewater reclamation is becoming a critical component of water management in meeting the increased water demand in many areas where significant population growth and/or water shortages occur. As an alternative resource, treated wastewater can be used for a wide range of applications such as industrial, agricultural and domestic purposes depending on its quality. Membrane filtration is one of the most efficient and reliable technologies to produce high quality water, however membrane fouling, which can result in the irreversible loss of product water flux over time and reduced membrane life span, remains a critical factor limiting the use of the technology for wastewater reclamation.

Membrane fouling can be severe in the low pressure membrane filtration of municipal secondary effluent for wastewater reclamation due to a wide range of components present in the water being prone to fouling. Hydraulic and chemical membrane cleaning are common approaches to restore membrane performance; however, membranes exposed to repeated cleaning cycles face gradual reduction in flux recovery and degradation of membrane materials. As another means of mitigating membrane fouling, feed pre-treatment using chemical coagulants is usually applied to remove undesirable organic and particulate matter.

Ultrasound (US) has been commercialised for surface cleaning from lab-scale (e.g., laboratory cleaning baths and medical tools) to industrial applications (e.g., silicon wafers, and metal parts). A limited number of studies have been conducted using US as a means of mitigating membrane fouling over the last decade. Cavitation and acoustic turbulence generated by US are generally regarded as the major mechanisms of detaching particles and other foulants from membrane surfaces.

US techniques have also been used for the dispersion of agglomerated particles in the liquid phase. Several researchers reported that US can also alter the surface properties of organic molecules due to ultrasonic cavitation forces (Yang et al., 2008; Laurent et al., 2009). Rapidly collapsing cavities generate shear forces that can break polymer chains

(Szu et al., 1986; Czechowska-Biskup et al., 2005). For instance, it was found that polysaccharides (eg., chitosan and starch) were degraded by US, leading to a reduction in molecular weight (Czechowska-Biskup et al., 2005). Moreover, it was proved that the heat from cavity implosion decomposed water into hydroxyl radicals which are highly oxidative toward organics (Suslick, 1989).

US has been examined as a feed pre-treatment for mitigating the fouling potential of the organic components present in a natural surface water (Tran et al., 2007). It was found that short term sonication (60 sec) diminished the flux decline for MF of the water, and membrane performance improved even more when the US treatment was followed by alum coagulation. However, there has been very little study on the application of the ultrasonic techniques in the low pressure membrane filtration of municipal wastewater.

The aim of this study was to investigate the effect of US on membrane cleaning and feed pre-treatment for fouling mitigation in the microfiltration of a biologically treated municipal effluent. In this lab-scale study, membrane performance was evaluated by measuring permeate flux, flux recovery after backwashing, and changes in water quality. Further analyses of membrane surfaces and organic matter in the solution were conducted to obtain a better insight into the effect of US on membrane performance.

The thesis is structured as follows. Chapter 2 is the literature review which describes the municipal wastewater treatment process including biological treatment, the characteristics of the biologically treated wastewater, and the fouling of membranes during low pressure filtration. Coagulation used as pre-treatment for membrane filtration, the principles of ultrasonication and related studies utilising this technology for membrane water and wastewater treatment are also reviewed. The materials and methods employed in this study are introduced in Chapter 3. Chapter 4 contains the results and discussion of the investigation of the effect of US on cleaning membranes fouled with an activated sludge-lagoon effluent. Chapter 5 reports on the impact of feed pre-treatment using US alone and US followed by Al^{3+}-based coagulation on the performance of microfiltration. The major outcomes from this study are summarised in chapter 6, and some recommendations for future work are outlined.

Chapter 2. Literature review

2.1 *Introduction*

This chapter describes challenges in the use of membrane technology for wastewater treatment (section 2.2), and pre-treatment and cleaning methods used in low pressure membrane filtration (section 2.3–2.4). Chemical and physical phenomena induced by ultrasonic irradiation of aqueous solutions are detailed in section 2.4 and its application for membrane fouling control and cleaning is described in section 2.5. The findings in the literature are briefly summarised in section 2.6.

2.2 *Wastewater treatment*

2.2.1 Contaminants in municipal wastewater

Municipal wastewater contains a wide range of contaminants which are derived from sewage discharged from domestic, commercial and industrial sources. These contaminants, comprising both inorganic and organic matter, are present in soluble, particulate and colloidal forms. Colloids are defined as fine suspended particles in the size range of a few nanometres to a few micrometres which includes 1) inorganic: clay, silica and metal oxide, 2) organic: agglomerated natural and synthetic organics, 3) biological: bacteria and other micro-organisms (Al-Amoudi and Lovitt, 2007). The composition and the contamination level of the wastewater vary significantly depending on location and season. Major constituents in municipal wastewater can be classified into six different categories (Table 2-1).

Table 2-1 Components in wastewater and their effects on health and the environment (Henze, 2002; Pescod, 1992; Shon et al., 2006)

Major group	Component	Health risk and environmental effect
Micro-organisms	Pathogenic bacteria, viruses, protozoa and helminths	Risks when bathing and eating shellfish
Biodegradable organic materials	Amino acids, proteins, glucose and carbohydrates	Oxygen depletion in rivers, lakes and fjords, changes in aquatic life (less diverse)
Other organic materials	Detergents, pesticides, fat, oil and grease, colouring, solvents, phenols, cyanide	Toxic effect, aesthetic problem, bio-accumulation
Nutrients	Nitrogen, phosphorus, ammonia	Eutrophication, oxygen depletion, toxic effect
Metals	Hg, Pb, Cd, Cr, Cu, Ni	Toxic effect, bio-accumulation
Other inorganic materials	Acids (e.g., hydrogen sulphide), bases	Corrosion, toxic effect

2.2.2 Wastewater treatment plant processes

Collected wastewater is treated in a wastewater treatment plant (WWTP) in the following sequence. Firstly, large inorganic solids and floating matter (> 10 μm, e.g., sand) are removed in a preliminary treatment, which consists of screens and grit chambers. In the following primary treatment, the majority of suspended solids are removed in sedimentation tanks or clarifiers. In secondary treatment, biological processes (e.g., biofilters and activated sludge) are employed to remove oxygen-demanding organic matter and dissolved organic components. Figure 2-1 shows a typical activated sludge plant which consists of aeration tanks and a settling tank. The biological processes are carried out by various organisms, including bacteria, fungi, algae, protozoa and metazoa (Henze, 2002) where the dissolved organic matter is partially adsorbed by biological flocs and degraded to carbon dioxide. Treated organic matter is discharged in 3 different forms: a) carbon dioxide, b) excess sludge or c) the effluent (Henze, 2002). In conventional activated sludge processes, biological flocs are separated in a clarifier by sedimentation, however, the effluent may contain a large

amount of particulates and colloids (Wilf and Alt, 2000). In addition, the biological activities produce soluble microbial products (SMPs) and extracellular polymeric substances (EPS) which are regarded as toxic and inhibit nitrification (Shon et al., 2006). The treated effluent undergoes further processes to remove the residual matter, where lagoon treatment and/or filtration is performed to meet the quality of product water for reuse.

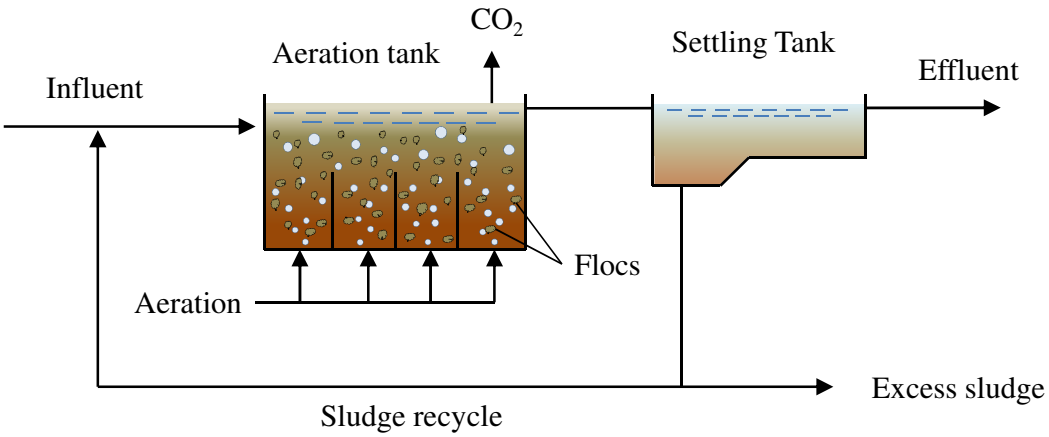


Figure 2-1 Activated sludge process elements

2.2.3 Membrane systems

Membrane filtration systems for effluent treatment comprise pressurised or immersed membrane units, backwashing and chemical cleaning systems and air scour systems. For pressurised membrane configurations, membranes are located in pressure vessels and multiple sets of the vessels are assembled into membrane units. Backwashing is conducted by flushing in the reverse direction (from permeate to feed side) using a small amount of product water. To enhance backwashing, occasionally chemical agents are injected during the process. When the transmembrane pressure (TMP) cannot be restored by a regular operating protocol, intensive chemical cleaning is performed, so-called cleaning-in-place (CIP). CIP is generally conducted for an individual membrane unit removed from operation. Types of chemical used in the cleaning processes depend on the types of foulants and membrane materials and are carefully selected taking membrane manufacturers' recommendations into account. Membrane types and their characteristics are shown in Table 2-2.

Concentration and backwash waste streams generated by low pressure membrane treatment are returned to upstream and are then treated by biological processes, or reuse options may be available depending on the quality (Water Environment Federation, 2005).

Table 2-2 Characteristics of materials for membranes used in wastewater treatment (Water Environment Federation, 2005; Donalson, 2009; Sumitomo electric fine polymer, 2011)

	Materials (hydrophobicity)	Advantages	Disadvantages (range)
Reverse osmosis / Nanofiltration	Cellulose acetate (hydrophilic)	Inexpensive and easy to fabricate	Poor thermal stability (< 30 °C) Poor chemical tolerance (pH 3–6) Poor mechanical stability High degradable
	Polyamide (hydrophilic)	Good thermal and chemical stability (pH 3–11) Great permeability	Sensitive to chlorine
Microfiltration / Ultrafiltration	Polypropylene (hydrophobic)	Withstand moderately high temperatures	Sensitive to chlorine Less resistant to chemicals Elongated pores Susceptible to oxidation
	Polysulfone Polyethersulfone (hydrophobic, able to be modified)	Good mechanical strength and thermal and chemical stability Excellent film forming	High hydrophobicity (sensitive to membrane fouling) broad pore size distribution Low tolerance of aromatic hydrocarbons or ketones
	Polyvinylidene difluoride (PVDF) (hydrophobic, able to be modified)	Autoclavable Good mechanical strength and solvent resistance	Less chemical resistance than Polytetrafluoroethylene
	Polytetrafluoroethylene (very hydrophobic, able to be modified)	Excellent organic resistance Excellent chemical stability to strong acids, alkalis and solvent Wide operating temperature range (-100 to 260 °C)	Only available in MF pore sizes Expensive
	Ceramic	High tolerance to chemicals and heat (pH 0–14)	Expensive

2.2.4 Membrane fouling in low pressure filtration of wastewater treatment

In general, membrane fouling mechanisms can be described as external surface fouling (i.e., cake/gel formation) and internal pore blocking. The organic fouling behaviour of low pressure membranes is generally consistent with that of membrane bioreactors (MBRs) (Amy, 2008). In the tertiary treatment of wastewater, organic fouling is significant and results from the accumulation and adsorption of the organic matter on the membrane surface and the pore walls (Zhu et al., 2010). Effluent organic matter (EfOM) is composed of a diversified group of substances containing high to low molecular weight species and so has a complex and heterogeneous nature. These organic components can be divided into three groups according to their sources (Jarusutthirak et al., 2002): 1) natural organic matter (NOM) which originates from drinking water sources, 2) synthetic organic compounds discharged from domestic use and disinfection by-products (DBPs) derived from water and wastewater disinfection, 3) SMPs produced during the biological process in wastewater treatment. Among these components SMPs, such as polysaccharides and proteins, are regarded as recalcitrant foulants causing severe flux decline and irreversible fouling for low pressure membrane filtration in wastewater treatment (Jarusutthirak and Amy, 2006; Fan et al., 2008). These materials exist in both colloidal and macromolecular forms (Amy, 2008).

2.2.5 Factors which influence membrane fouling

There are many factors which influence membrane fouling, but they can be divided into three categories: feed properties, membrane characteristics and operating conditions. The interactions between EfOM and membranes which affect fouling potential are surface charge, hydrophobicity and pore size of the membrane, and particle size/molecular weight (MW) of EfOM. Membranes with narrow pore size distribution, smooth hydrophobic nature and high porosity are generally considered to have lower fouling potential (Le-Clech et al., 2006).

a. Hydrophobic interaction

The hydrophobic interactions of foulants and membranes in MBRs were reviewed by Grander et al. (2000), Chang et al. (2002), Le-Clech et al. (2006) and Meng et al. (2009). The permeate flux can be affected by the hydrophobic interactions of membrane and

feed components, and generally fouling occurs readily on membranes having greater hydrophobic nature due to increased interaction between EfOM and membranes. Membrane modification has been intensively studied to improve fouling resistance by surface treatment (e.g., sulfonation) (Baroña et al., 2007), and blending/immobilising with polymeric (Jung, 2004) and inorganic materials (e.g., TiO_2) (Bae and Tak, 2005). These successfully increased flux and mitigated irreversible fouling by protein solutions and activated sludge liquors.

b. Electric repulsion

Greater negative charge of membranes reduces EfOM fouling (Jarusutthirak, 2002). Most of the organic substances present after activated sludge processes (e.g., NOM, EPS and bacterial cells) have a negative charge (Meng et al., 2006; Le-Clech et al., 2006). These materials contain a large proportion of anionic functional groups such as carboxylic and phenolic groups (Hong and Elimelech, 1997) and thus are repelled by negatively charged membranes.

c. Relationship between size of membrane pores and particles

There is a strong correlation between membrane pore size and particle size distribution of feed solution and the degree of membrane fouling (Le-Clech et al., 2006). Where foulants are smaller than the pore size of the membrane, internal membrane fouling will be dominant. This causes rapid pore blockage and marked reduction in filtration performance (Lim and Bai, 2003). When the particle size is similar to the pore size of the membrane, pore blockage becomes more complete which leads to a dramatic reduction in the filtration performance (Zhang et al., 2008). Lee et al. (2004) investigated the fouling behaviour of NOM in MF and UF using several surface waters and suggested that the larger MW components (i.e., macromolecular compounds and colloidal organic matter) have more influence on flux decline in low-pressure membrane filtration. A more significant flux drop and lower flux recovery observed for MF was attributed to pore blockage associated with the large-MW compounds, whereas the fouling mechanisms for UF were cake layer formations.

d. Roughness of membrane surface

In the later stage of fouling, membrane surface roughness or morphology can influence the degree of fouling. A larger amount of material can be adsorbed on a rougher surface compared to a smooth surface due to the larger surface area. In addition, foulants deposited in the dents are exposed to less hydraulic shear force, thus severe fouling occurs in these spots (Li et al., 2007). Lee et al. (2004) confirmed that increased adsorptive fouling was observed with increasing surface roughness of the membranes in the filtration of surface water. A similar result was observed for the filtration of EPS by Zhang et al. (2008).

In addition to the fouling mechanisms above, more factors have been reported and interactions of these make it more complicated. In particular, soluble and colloidal forms of protein-like and polysaccharide-like materials have been intensively studied to acquire a better understanding of fouling mechanisms in the filtration of biologically treated effluent. Proteins are unstable and have heterogeneous natures and structures and interact with a membrane surface through dipole interaction. Hydrogen bond formation between polysaccharides and membrane materials also affect the filtration performance (Amy, 2008). Furthermore, a recent study reported that the mixture of proteins and polysaccharides can develop network structures which have high filtration resistance (Susanto et al., 2008). These biopolymers form a highly hydrated gel matrix on the membrane surface, providing a nutrient for biofilm formation and thus can contribute to significant flux decline (Henze, 2008).

2.3 *Fouling mitigation*

2.3.1 Pre-treatment for membrane filtration

As mentioned earlier, biologically treated wastewater effluent contains various contaminants with multiple characteristics which leads to complex mechanisms in membrane fouling. Moreover, effluent quality parameters vary depending on the contaminant levels at the intake, season and condition of activated sludge processes etc. Consequently, many operating parameters (e.g., feed flux, duration of filtration and backwashing, cleaning agents and frequency) should be considered to control membrane fouling and prolong the life span of the membranes. Membrane systems are

reliable but the units are costly, therefore pre-treatment can be useful to maintain system performance.

2.3.1.1 Chemical coagulation

Coagulation and flocculation are the processes used to clarify water by addition of a chemical agent, which destabilises fine suspended matter and encourages the particles to form aggregates (i.e., flocs). Efficiency of separation can be improved by increasing the size of the impurities. Coagulation and flocculation can be an effective pre-treatment to maximize the performance and life of membranes since fine particles and colloids, which generally cause severe flux drop, are destabilised, then form larger flocs and are eventually removed prior to the membrane filtration. Furthermore, some cases showed that coagulation could reduce irreversible membrane fouling. Farahbaksh et al. (2004) suggested that the improvement of foulant removal was due to the reduction of pore blocking by increasing the size of the particulate matter. The adsorption or entrapment of problematic organic substances in the coagulation flocs and the formation of the cake layer consisting of the flocs on the membrane surface could prevent these materials from direct deposition onto the membrane surface (Chen et al., 2007; Fan et al., 2008).

Hydrolysing metal salts such as aluminium sulphate (alum) and ferric chloride are widely used in water and wastewater treatment processes. Due to the strong charge of the metal cations, water molecules in direct contact with the metal ions are polarised and hydrogen ions are progressively released into water. A simple hydrolysis sequence for cationic metals is given as follows:

$$M^{3+} \leftrightarrow M(OH)^{2+} \leftrightarrow M(OH)_2^{+} \leftrightarrow M(OH)_3 \leftrightarrow M(OH)_4^{-} \qquad \text{Equation 2.1}$$

where M is metal atom

This equilibrium proceeds from left to right with increasing pH of the solution. As both aluminium and iron hydroxide have very low solubility around neutral pH, amorphous precipitates are produced (Duan and Gregory, 2003). In addition to monomeric species, many polynuclear formations can be produced, such as dimer ($Al_2(OH)_2^{4+}$), trimer

($Al_3(OH)_4^{5+}$), and tridecamer ($Al_{13}O_4(OH)_{24}^{7+}$) for aluminium. Many researchers considered tridecamer "Al_{13}" as the most effective species for removing impurities due to its stability and high positive charge (Jiang, 2001; Duan and Gregory, 2003). The Keggin structure of Al_{13} is a tetrahedral Al O_4^{5-} linked with 12 other Al octahedra with shared edges (Bottero et al., 1987).

The production of specific prepolymerised coagulant species has drawn interest. Advantages of the prepolymerised coagulants are their applicability over wide ranges of pH and temperature of solution (Bratby, 2006), lower dose requirement and lower amount of residual metal ions (Jiang, 2001). Gregory and Dupont (2001) compared the characteristics of flocs produced by alum and polyaluminium chloride (PACl) in the treatment of a clay suspension and the PACl flocs were larger and stronger than the alum flocs. Similar results were obtained for iron, where the stability of polyferric sulphate flocs was greater than the monomeric $FeCl_3$ flocs (Cheng, 2002).

2.3.1.2 Mechanisms of coagulation

Hydrolysing coagulants act by one of two mechanisms for the destabilisation of particulate and colloidal matter: charge neutralisation and sweep flocculation. Under charge neutralisation conditions, positively charged metal hydrolysing products reduce the surface charge of the suspended matter, thus inducing precipitation and agglomeration (Jiang, 2001). Charge neutralisation occurs between the hydrolysing metals and the contaminants with a negative charge only at very low coagulant dosages. This event involves three steps: 1) nuclear formations of aluminium/iron hydroxide species, 2) deposition of hydroxide species onto colloidal surfaces, and 3) aggregation of neutral particles (Duan and Gregory, 2003). However, excessive dosage causes charge reversal and the particles are thus re-stabilised. The optimum dosage of coagulant will be in an extremely narrow range and particle aggregation will be slow for a solution with a low level contamination. Therefore, charge neutralisation may be not suitable in practical processes. On the other hand, sweep flocculation can be faster and reliable for destabilisation of impurities. Sweep flocculation, which utilises coagulant doses much higher than charge neutralisation, enhances precipitation of Al amorphous hydroxide and floc growth. Contaminants are entrapped in the growing hydroxide

precipitates which gives a marked increase in particle removal compared with charge neutralisation (Duan and Gregory, 2003). The flocs produced by sweep flocculation are generally larger and easily settled.

2.3.1.3 Impacts of coagulation on membrane filtration

Applying coagulation and sedimentation as a pre-treatment for filtration brings significant improvement in permeate flux because destabilised particles, colloidal matter and solutes which can adsorb to coagulant precipitates are separated from the feed. However, in some cases a settling process after coagulation proved unnecessary as it did not achieve a further improvement in permeate flux. Carroll et al. (2000) investigated the effect of alum pre-treatment on MF performance for surface water and observed that the settleable flocs have little effect on decline in permeate flux. Similar results were obtained for a biologically treated effluent, the substances that were not removed during settling showed significant filtration resistance to MF (Fan et al., 2008). Other cases showed that coagulation exacerbated membrane fouling. Howe et al. (2006) used alum and ferric sulphate as pre-treatment for MF and UF for surface water and greater flux decline was observed for MF, while the flux for UF was improved significantly. This result also indicated that there is a direct correlation between pore sizes of the membranes and the size of residual contaminants influencing filtration performance. On the other hand, even if the flocs formed are very small and are not effectively removed by a settling stage, the permeate flux improves due to the modified adsorption characteristics caused by surface neutralisation (Kim et al., 2005). Moreover, irreversible fouling may not be completely eliminated by coagulation unless all dissolved compounds are removed from the solution (Huang et al., 2009).

As indicated earlier, due to its ability to produce settleable flocs, sweep flocculation is preferable to charge neutralisation when separating the flocs by conventional sedimentation or sand filtration. The use of coagulation in in-line membrane systems (i.e., without a settling process) is different from when sedimentation is used. In the hybrid coagulation-filtration system, feed is directly introduced into the membrane systems after the coagulation, and a cake layer which is formed on the membrane has high porosity and is readily removed by hydraulic cleaning (Lee et al., 2000; Chapman

et al., 2002; Choi and Dempsey, 2004). Therefore, the factors influencing membrane fouling in the in-line systems will be the size of the flocs, the morphology/porosity and compressibility of the cake layer, the affinity between the flocs and the membrane materials, as well as removal of the contaminants. Several studies showed that the flocs formed by charge neutralisation are smaller (Chakraborti et al., 2000), less compressible and have higher porosity than sweep flocculation (Lee et al., 2000; Choi and Dempsey, 2004; Li et al., 2006; Wang et al., 2010).

The removal of turbidity and organic solutes is significantly influenced by dosage of coagulants and the pH conditions. Turbidity was effectively removed by sweep flocculation at neutral pH, while reduction in UV_{254} was better under slightly acidic conditions (Choi and Dempsey, 2004). However, other research found that dosing under acidic conditions produces small flocs which cause severe membrane fouling by plugging or adsorption to the membranes (Kimura et al., 2008).

Wang et al. (2008) investigated the effect of size and structure of monomer and polymer flocs on MF performance for humic acid solution. Although prepolymerised coagulants are less pH sensitive and the dosage requirement was 60–70% less than alum, the cake layer resistance after treating feed with polyaluminium hydrate (ACH) and PACl was higher than with monomeric alum, which was attributed to the higher floc density. They concluded that ACH and PACl were not well suited for use in coagulation-MF hybrid systems.

Clearly, coagulant type, dosage and pH of the solution should be carefully selected according to the characteristics of targeted contaminants and membrane materials.

2.3.2 Membrane cleaning

During the operation of membrane systems, periodic cleaning is required to control membrane fouling. Hydraulic backwashing is a commonly used method which removes the accumulated layer on the membrane surface. The typical backwashing cycle takes approximately 3 min at intervals of 10–30 min and is initiated at a predetermined TMP increase (Water Environment Federation, 2005). Optimum backwashing protocols with

variables of backwash duration and flux, cross-flow velocity, TMP and chemical addition need to be determined depending on the fouling characteristics of the contaminants. To control biological growth on the membranes, sodium hypochlorite is commonly added to backwashing water (Crittenden et al., 2005). In CIP, the most common chemical agent is sodium hypochlorite and caustic soda which effectively removes biological foulants deposited on the membrane surface (Brant et al., 2010). Citric acid can be applied for the cleaning of mineral scale caused by the increased solution pH due to the emission of CO_2 during the biological treatment, and hydrochloric acid and surfactant are also used occasionally (Water Environment Federation, 2005).

2.4 *Features of ultrasound*

The definition of ultrasound is an acoustic wave with a frequency above 20 kHz, which is greater than the upper limit of human hearing. Ultrasound creates alternating regions of compression and rarefaction in the medium (Mason, 1997). In a liquid phase, the acoustic energy is absorbed in the medium and generates a flow, so-called acoustic streaming.

When the amplitude of acoustic pressure exceeds the tensile strength of the liquid, cavity nuclei are formed within the liquid, however, under practical conditions less stress force will be needed to form cavities for most liquids due to the presence of dissolved gases or contaminants acting as cavitation nuclei (Leighton, 1997). If sufficient energy is supplied, the cavities absorb energy and grow gradually during a sequence of contraction and expansion (Suslick, 1989). The critical size (i.e., maximum size to which the bubbles can grow) increases with increased acoustic frequency (Pétrier and Francony, 1997) and growth speed increases with increasing ultrasonic intensity (Suslick, 1989). The number of cavities produced by ultrasound increases with increasing ultrasonic intensity (Sivakumar and Pandit, 2001).

When the cavity reaches the critical size, aggressive implosion occurs, which induces some unique chemical and mechanical effects. Cavitation occurs over the frequency range of 20–1000 kHz (Kyllönen et al., 2005). Furthermore, microstreaming is induced

at the boundary of bubbles and liquid due to the bubble oscillations and so agitates the liquid. These features mean that ultrasound techniques are utilised in various apparatus from laboratories to large industries for processes such as dispersion and emulsification, cleaning and extraction (Kyllönen et al., 2005). Most of the effects utilising ultrasound are attributed to multiple mechanisms.

2.4.1 Physical stress caused by cavitation

Leighton (1997) reviewed the mechanisms of physical erosion caused by acoustic cavitation, shock wave emission and micro-jet. A shock wave is the pressure pulse emitted when cavities implode. The pulse emitted by a single cavity may only affect the area within the radius of the cavity; gathering a large number of bubbles emphasizes their effects, passing the released energy on to adjacent bubbles. As a result, the centre of "cloud cavitation" has a higher energy than an original bubble. When a cavity collapses near a large solid surface, an implosion occurs asymmetrically, expelling a liquid jet (so-called micro-jet) towards the wall at more than 100 metres per second (Suslick, 1989; Mason, 1997). The intensity of shear force produced by cavitation increases with increasing number of collapsed cavities and increasing bubble size, thus higher intensity and lower frequency applied to the system generates more vigorous physical forces (Tiehm et al., 2001).

2.4.2 Chemical reaction induced by cavitation

The collapsed cavity generates extremely high pressure and heat (i.e., a hot spot) which diffuses immediately and heats the liquid in the vicinity (Suslick, 1989). This extremely high temperature and pressure derived from the cavitation decomposes water molecules into hydroxyl radicals ($OH^{\bullet}$) and hydrogen atoms (H^{+}) (Riesz and Kondo, 1992). These radical species are highly reactive toward organic compounds, oxidising and decomposing them into smaller molecules. The sonochemical reaction occurs inside the cavities and/or at the interface between the cavity and the bulk solution where the extreme conditions are produced (Mason, 1997).

2.5 *Ultrasound in membrane filtration*

Various studies have been conducted using US as a means of mitigating membrane fouling over the last decade. Several types of feed solutions were investigated, including organic compounds: dextran, milk, carboxyl cellulose, latex particles as well as inorganic matter (Fe^{+3}, $CaSO_4$, and silica). The US frequency applied was in the range of 20–1000 kHz and power intensity was up to 1500 W. Cavitation and acoustic turbulence generated by US are generally regarded as the major mechanisms of minimizing foulant deposition and detaching particles and other foulants from membrane surfaces. Lamminen et al. (2004) simplified the effects of ultrasound on membrane cleaning in a schematic illustration (Figure 2-2).

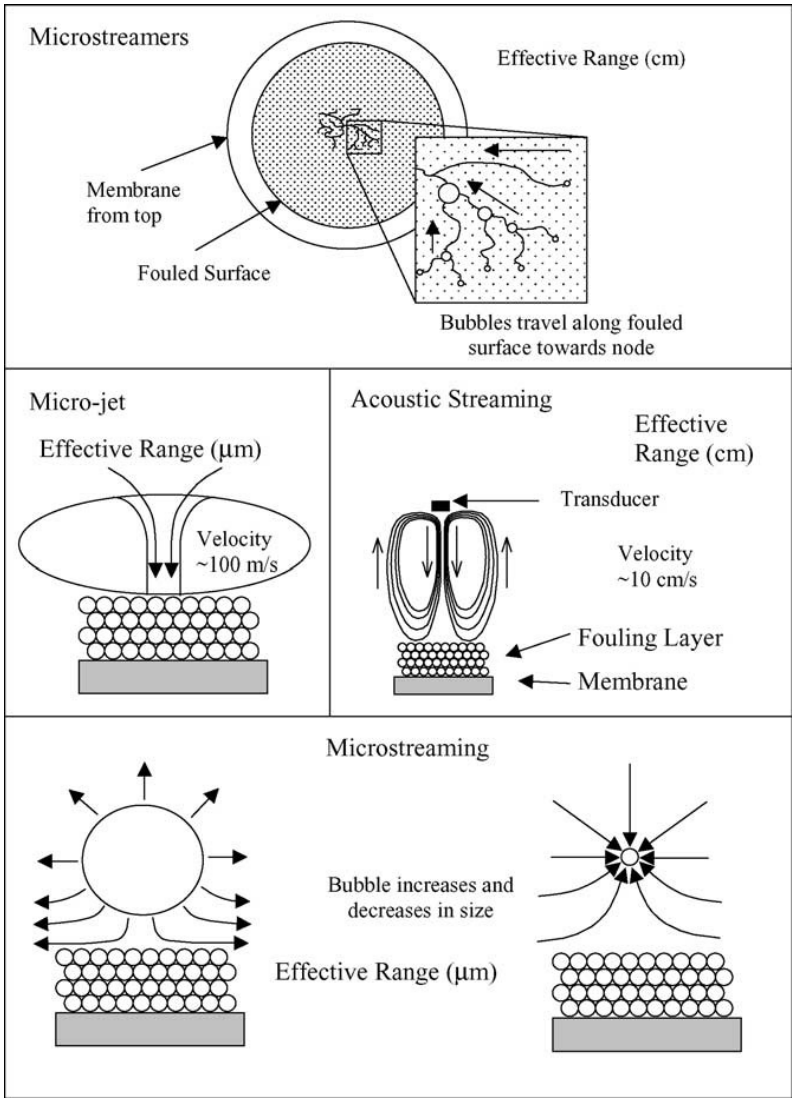


Figure 2-2 Possible mechanisms of ultrasonic effects on particle removal and detachment (Lamminen et al., 2004)

2.5.1 Ultrasonic online fouling control and membrane cleaning

One application of ultrasound for membrane filtration is as an online membrane fouling control system, which has an ultrasound transducer located either internal or external to the filtration cell and which operates during the filtration process. The advantage of this is that there is no interruption of filtration. US has also been applied to membrane cleaning to restore membrane performance, which was conducted simultaneously with hydraulic or chemical cleaning, or in a batch external cleaning vessel. The parameters studied were intensity and frequency of US, feed properties, temperature and operating pressure, all of which influence the efficacy of ultrasound on membrane filtration. The impacts of each parameter on both enhancing filtration and cleaning have common features.

Power intensity was investigated by Kobayashi et al. (1999), Lamminen et al. (2006), and Cai et al. (2009). Intensity was generally expressed as output of the US transducer (W) or divided by the unit area of the transducer (W cm^{-2}). Ultrafiltration (UF) of *Radix astragalus* extract (a solution containing polysaccharides, saponins and flavonoids) was conducted in the US field (output power range of 10–120 W) and higher US intensity led to better filtration performance. Kobayashi et al. (1999) reported that similarly for filtration of dextran using polyacrylonitrile UF membrane, the permeate flux increased with increasing ultrasound intensity at low frequencies (28 and 45 kHz). However, there was no flux improvement with increased power intensity at 100 kHz. Lamminen and his co-workers (2006) examined a cross-flow system with an embedded transducer (476 kHz) for filtering a solution containing latex particles. They quantified the intensity of cavitation by measuring the production of hydrogen peroxide and detection of sonoluminescence. The results proved that increased intensity increased the amount of H_2O_2 over the applied range of 3.3–15.5 W as well as the cavitation zone (i.e., effective area of US). This resulted in a dramatic increase in permeate flux, however, damage to the membrane materials was reported at high intensity. In terms of energy consumption and durability of membrane, short bursts of US around 10 min (Muthukumaran et al., 2004) and intermittent ultrasound with pulsing for 1sec on and 10 sec off (Lamminen et al., 2006) were found to be a cost efficient and beneficial way to operate the system.

Frequency of US may be one of the most influential parameters for fouling control as it is the determining factor for the size of bubbles and intensity of cavitation. It was found that lower frequencies are more effective for both enhancing filtration performance and membrane cleaning, which is consistent in most of the reports (Kobayashi et al., 1999; Kobayashi et al., 2003; Lamminen et al., 2006; Muthukumaran et al., 2007; Cai et al., 2009). Permeate flux was significantly improved by US at a frequency of 28 kHz in UF of peptone solution and MF of milk solution, but little effect was obtained at 100 kHz (Kobayashi et al., 2003). Lamminen et al. (2006) used US at even higher frequency (476 kHz) than Kobayashi et al. (2003), and a dramatic increase in permeate flux was obtained for filtration of latex particles as mentioned above. The different results may be due to different configurations of the US transducer (i.e., ultrasonic bath compared with embedded transducer internal filtration cell), solution content and membrane materials.

High frequency (1 MHz) pulsed US was investigated for its effect on UF of whey solution and severe irreversible fouling was observed when US was performed during filtration under a high transmembrane pressure (300 kPa). Greater irreversible fouling occurred than without sonication, which was not seen in the filtration with 50 kHz continuous US (Muthukumaran et al., 2007). The authors suggested that the greater fouling was due to higher cake layer compaction or deposition in the membrane pores resulting from particle agglomeration and/or denaturation of whey caused by US irradiation.

At lower US frequency bubble implosion is more violent than at higher frequency, and the cleaning efficiency is thus greatly improved by the physical shear force induced in the US field. At high frequency, although the cavitation is less violent, larger concentrations of radical species and hydrogen peroxide are generated (Pétrier and Francony, 1997), these could cause chemical reactions with organic and inorganic components present in the feed. This could change the propensity for membrane fouling by modifying the properties of foulants.

Sui et al. (2008) investigated the effects of US as an on-line fouling control in an anaerobic membrane bioreactor. Although increasing sludge concentration required longer sonication time, US with frequency of 28 kHz and intensity of 0.122 W cm^{-2} effectively controlled membrane fouling. After 28 days of filtration with intermittent US (irradiation interval varied from 1 to 5 min per hour), the filtration resistance was less than one third of that without US. However, US may have a slight negative impact on the activity of the anaerobic bacteria, even though chemical oxidation demand (COD) removal was stable.

Kang et al. (2006) tested US membrane cleaning in pilot-scale filtration of glass industry wastewater. US cleaning achieved high flux recovery (more than 90%), which was more effective than any of the chemicals tested (HCl, NaOH, citric acid, ethylene diamine tetra acetic acid (EDTA) and NaOCl) for membranes fouled with a clay-glass particles mixture. The use of US boosted the effectiveness of NaOH cleaning, the flux recovery of more than 95% was nearly 40% higher than without US. The synergistic effects of US with chemical agents were also reported by Popović et al. (2010) and Muthukumaran et al. (2004). They both suggested that energy consumption of US could be traded off by providing higher cleaning efficiency and less chemical consumption.

Changes in rejection of dissolved organic matter caused by US were investigated for the filtration of NOM and silica by Chen et al. (2006). On-line US enhanced permeate flux dramatically, however rejection of dissolved organic matter was decreased. The decline in rejection was attributed to the decreased steric exclusion caused by removing the fouling layer. It was also suggested that the increased charge exclusion caused by deposition of NOM on the membrane in the absence of US might have been related to the reduction in rejection. On the other hand, Feng et al. (2006) observed a marginal reduction in rejection caused by US for filtration of $CaSO_4$, Fe^{3+} and carboxymethyl cellulose by reverse osmosis membrane. No other research reports noted change in the quality of the permeate unless the membrane was damaged by sonication.

The position and direction of US transducers applied to membranes was studied in crossflow membranes (Kobayashi et al., 1999). When the transducer was placed on the feed side (i.e., fouling surface faced the transducer) the permeate flux was higher than

when placed on the permeate side. It should be noted that when the sonic waves are propagated from one medium to another, the energy can be partially reflected. Therefore, the configuration of US transducers is also important so as to not reflect a large amount of energy.

2.5.2 Applications of ultrasonic technology for water and wastewater treatment

Ultrasound has been investigated as an advanced oxidation process (AOP) for wastewater treatment, as ultrasonic irradiation of aqueous solutions generates free radical species which can oxidise dissolved organic compounds. Degradation is induced as in the following equations (Pétrier et al., 1994; Naddeo et al., 2009; Mahamuni and Adewuyi, 2010):

$$H_2O \xrightarrow{)))} HO\bullet + H\bullet \qquad \text{Equation 2.2}$$

$$H\bullet + O_2 \xrightarrow{)))} HOO\bullet \qquad \text{Equation 2.3}$$

$$2HO\bullet \xrightarrow{)))} H_2O_2 \qquad \text{Equation 2.4}$$

$$2HOO\bullet \xrightarrow{)))} H_2O_2 + O_2 \qquad \text{Equation 2.5}$$

$$\text{Pollutants} + HO\bullet \rightarrow \text{degradation products} \qquad \text{Equation 2.6}$$

$$\text{Pollutants} + HOO\bullet \rightarrow \text{degradation products} \qquad \text{Equation 2.7}$$

$$\text{Pollutants} + H_2O_2 \rightarrow \text{degradation products} \qquad \text{Equation 2.8}$$

where

))) is ultrasonic irradiation

Nasseri et al. (2006) investigated the effect of US (25 W cm^{-2} output) at frequencies of 35 and 130 kHz for the decomposition of organic matter in wastewater secondary effluent. US at the frequency of 130 kHz generated 2.5 times as much H_2O_2 as US at 35

kHz, which resulted in a greater reduction of total chemical oxygen demand in the solution. On the other hand, a larger amount of suspended COD was converted to soluble COD at the lower frequency. There was no significant effect of US on either mineralisation or enhancing the biodegradability of dissolved organic matter for 60 min US exposure. Contrary to the results obtained by Nasseri et al. (2006), Naddeo et al. (2007) observed a strong capacity of high intensity-low frequency US (6.3–42.4 W cm^{-2}, 20 kHz) for NOM removal with the removal of up to 38% humic acid.

The degradation of phenol and carbon tetra-chloride (CCl_4) was compared by Pétrier and Francony (1997). The degradation rate of CCl_4 increased with increasing US frequency (20–800 kHz) and was faster than for phenol, while the optimum frequency for phenol degradation was 200 kHz. The authors suggested that the degradability was related to the volatile nature of these compounds. The hydrophobic and volatile CCl_4 can vaporise and react inside the cavities, therefore increase in number of bubbles increased mineralisation of CCl_4. However the decomposition of the hydrophilic phenol occurred in the bulk solution, therefore the reaction would depend on the amount of H_2O_2 released in the liquid phase.

Naffrechoux et al. (2000) studied the combination of ultrasound and UV irradiation (sonuv) for sewage treatment. Although the sonuv treatment achieved 50% reduction in COD of the municipal wastewater, it required 4 h treatment. Many researchers noted that sonochemical treatment for the decomposition of organic substances was not very efficient compared to the other oxidation processes such as ozonation (Mahamuni and Adewuyi, 2010).

Feed pre-treatment using ultrasound was conducted as a means of reducing the membrane fouling potential of the organic components present in a natural surface water (Tran et al., 2007). The aim was to modify the surface properties of contaminants so that they were less attracted to membrane materials. Short term and high intensity US (60 sec 1500 W at 20 kHz) diminished the flux decline for MF, and membrane performance improved even more when the sonication was followed by alum coagulation.

2.6 *Summary of literature review*

Membrane filtration is a reliable technology for providing water with consistent quality. However, membrane fouling is a major issue and unavoidable. Biologically treated municipal wastewater effluent contains various compounds derived from domestic, commercial and industrial sources as well as biological activity, which cause a significant decline in water productivity and membrane life. Factors affecting fouling are surface charge and hydrophobicity of membrane materials and contaminants, and pore size of the membranes and size distribution of impurities.

There are two approaches to mitigating membrane fouling: feed pre-treatment and membrane cleaning. Coagulation using Al^{3+} and Fe^{3+}-based coagulants is an effective pre-treatment (in terms of performance and economy) to destabilise colloidal matter and high molecular weight compounds and so form large agglomerated flocs. Coagulation also enhances permeate flux by producing a high porosity cake layer which can be readily detached by hydraulic cleaning and so enhance flux recovery.

In addition to regular backwashing, intensive chemical cleaning with NaOH and/or sodium hypochlorite is typically used for removing organic foulants from the membrane. In order to reduce amount of product water for membrane cleaning and consumption of chemical agents, in-line ultrasound was investigated and it was discovered that US at low frequency has a great effect on mitigating fouling. The detachment of fouling was attributed to the acoustic turbulence and the shear force generated during the implosion of cavities.

Furthermore it was discovered that sonication could degrade some of the organic materials and modify the characteristics of organic compounds to make them either less or more adsorbable. However, the degradation of organic substances required high power intensity and long term sonication. The modification of the surface properties of organics using short term US for changing the adsorption characteristics could be alternative way to mitigate membrane fouling

US has been studied for application to water and wastewater treatment, however detailed mechanisms for controlling membrane fouling, enhancing fouling detachment

and changing adsorption characteristics are not well established. In particular, little investigation has been conducted on its use in municipal wastewater reclamation. Therefore, further investigation is needed for better understanding of the effect of US on fouling mitigation for EfOM.

2.7 *Research objectives*

The objectives of this project were:

- To compare the effectiveness of US cleaning with hydraulic backwashing for foulant detachment in the microfiltration of biologically treated municipal wastewater effluent.

- To examine the change in characteristics and fouling potential of EfOM after US feed pre-treatment.

- To investigate the changes in the feed properties due to US treatment which affect aluminium coagulation and subsequent filtration performance.

In this lab-scale study, membrane performance was evaluated by measuring permeate flux, flux recovery after membrane cleaning using backwashing and/or US cleaning, and changes in water quality. A bath with US frequency of 45 kHz was chosen as it can induce powerful cavitation and shear forces, as observed in the literature.

Chapter 3. Materials and methods

This chapter provides details of the materials and methods used in this study. The characteristics of the feed water samples, membrane and chemical coagulants are detailed in Sections 3.1 to 3.4. The protocols of pre-treatment including ultrasonic treatment (Section 3.5) and coagulation (Section 3.6), microfiltration (Section 3.7), and membrane cleaning (Section 3.8) are also provided. Section 3.9 covers the analytical methods employed for this study.

3.1 *Feed water*

The treated wastewater used in this study was collected from the Head of the Road Storage pond of the Western Treatment Plant at Werribee, Victoria, Australia, where more than 50% of Melbourne's sewage is treated by an activated sludge-lagoon process (Melbourne Water, 2011). After passing through anaerobic lagoons, the water is treated by an activated sludge process. This process involves feeding air (i.e., oxygen) into the primary treated sewage where bacteria consume organic constituents and develop biological flocs which settle easily in clarifiers. The water then passes through a series of lagoons where further treatment and clarification occurs. The treated effluent contains a wide range of organic constituents which are derived from domestic and commercial sources as well as the biological treatment.

Table 3-1 shows the characteristics of the raw effluent collected for the period September 2009 to May 2011. Each experiment was performed using two water samples collected on different dates to ensure consistency of the results. The samples were stored at 4°C to minimise change in their properties. All filtration experiments were conducted within 14 days of sample receipt. Previous experiments with the treated effluent from this plant demonstrated that there was little change in its properties over this period (Stork, 2008).

Table 3-1 Characteristics of the raw effluent

DOC ($mg\ L^{-1}$)	UV_{254} (cm^{-1})	Turbidity (NTU)	pH	Conductivity ($\mu S\ cm^{-1}$)
8-11	0.16-0.22	1-6	7.6-8.2	1800-1900

For experiments where the turbidity was adjusted to a desired value, a centrifuge (Sorvall RC5C, DuPont, USA) was used to obtain particulates and some colloids (depending on their diameter and density) from the effluent. To prevent compaction/agglomeration of the large particles, the particle separation was performed in two steps. Firstly the raw effluent sample was centrifuged at 8,622 ×g for 20 min to separate the large particles, and then the supernatant was centrifuged at 25,261 ×g for 20 min to collect the smaller particles. The collected particles were added to non-centrifuged raw effluent to adjust the sample turbidity.

3.2 *Membranes*

The membranes utilized in this study were modified polyvinylidene fluoride (PVDF) microfiltration membranes (VVLP Durapore) supplied by Millipore. The characteristics of the membrane are listed in Table 3-2. The membrane sheet was cut into discs to fit the filter cell (diameter of 44.5 mm).

Table 3-2 Characteristics of the membrane used this study (Millipore, 2011)

Structure	Symmetric
Nominal pore size (μm)	0.1
Mean thickness (μm)	125
Porosity (%)	70
Pure water flux ($L\ m^{-2}\ h^{-1}$) * 70 kPa, 22 ± 1°C	1770 ± 60

* Measured in this study

3.3 *Coagulants*

Two Al^{3+}-based coagulants, (poly) aluminium chlorohydrate (ACH, Megapac 23, Omega Chemicals) and aluminium sulphate hydrate (alum, Chem-supply), were selected as they are commonly used in water treatment. The alum stock solution was prepared by dissolving 10 g of $Al_2(SO_4)_3 \cdot 18\ H_2O$ in MilliQ water and making up to 100 mL.

3.4 *Pure water*

A Milli-Q Gradient A10 (Millipore) system was used to produce high purity water (Milli-Q water). The Milli-Q water met ASTM Type I Standard Specifications for Reagent grade.

3.5 *Ultrasonic pre-treatment*

Two litres of the wastewater was warmed to room temperature (20 ± 1°C) before each test and treated in an ultrasonic bath (Sonica ETH3200, Soltec, Italy) at a frequency of 45 kHz. The power intensity was measured as 107 W output by calorimetry (Mason et al., 1992) as described in Chapter 4. For US pre-treatment of the effluent samples, the temperature increased only slightly, up to 23°C after 300 sec sonication, hence the influence of temperature change on feed properties was negligible.

3.6 *Coagulation methods*

Chemical coagulation was conducted to investigate the effect of US treatment of feed water on the performance of conventional coagulation and subsequent microfiltration. The jar tests were conducted with a Phipps & Bird PB-700 JarTester and involved the addition of coagulant to 1 L of effluent. The dosage of coagulants (5 mg as Al^{3+}) was as for the studies conducted by Fan et al. (2008) and Goh et al. (2010) who had optimised alum and ACH coagulation using the effluent from the same origin. They showed that optimal coagulant dosage was 5 mg L^{-1} as Al^{3+} in terms of filtration performance and flux recovery after membrane cleaning. As the pH of the effluent samples was in an

appropriate range for coagulation, and relatively consistent over the study period, further pH adjustment was not conducted.

Figure 3-1 illustrates the coagulation treatment procedure. After the addition of coagulant, the solution was stirred at 200 rpm for one min followed by slow mixing at 30 rpm for 20 min, after which the water was subjected to microfiltration without settling.

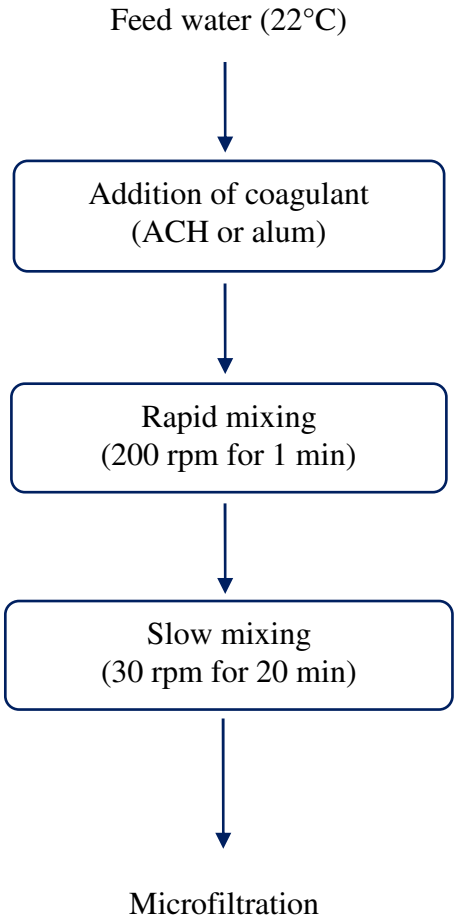


Figure 3-1 Experimental procedure for coagulation treatment

3.7 *Membrane filtration*

The membrane filtration unit comprised a feed tank and a stirred filtration cell with an effective membrane area of 13.4 cm^2 (Amicon 8050, Millipore); it was pressurised by

nitrogen gas at 70 kPa and stirred with a magnetic stirrer (KMO 2 IKA-Werke, Germany) at 430 rpm for a typical MF test. For the filtration of the effluent after coagulation, the stirring speed was reduced to 100 rpm to avoid breakage of flocs. The permeate volume was monitored every minute using an electronic balance (Sartorius BP 6100, Göttingen, Germany) connected to a computer for continuous data logging.

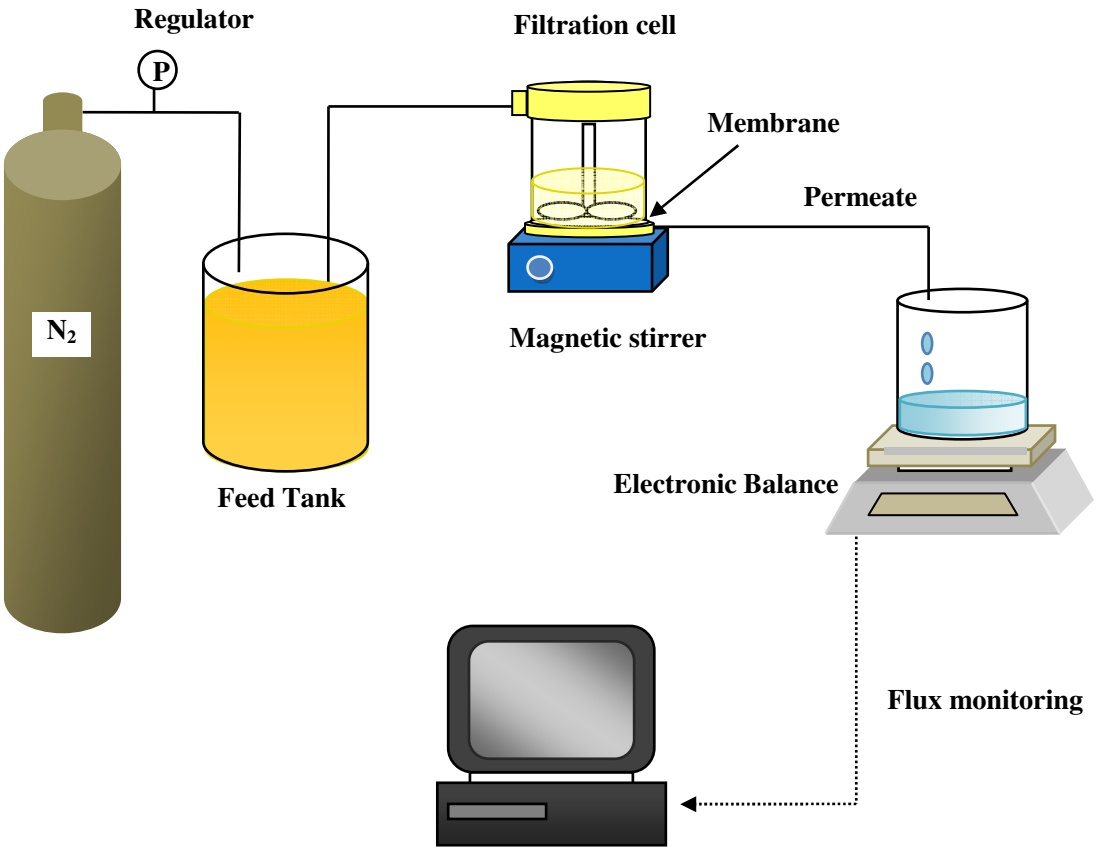


Figure 3-2 Diagram of microfiltration experimental setup

Before use, the MF membranes were soaked in Milli-Q water for 2 h after which approximately 300 mL of Milli-Q water was passed through each of the membranes used for tests. The pure water flux (J_0) was determined after the permeate flux stabilised. Membranes were selected for use when J_0 was in the range of 1770 ± 60 L m^{-2} h^{-1}. For US feed pre-treatment experiments, filtration was stopped when the permeate volume reached 500 mL. For the ultrasonic cleaning tests, fouled membranes were prepared by filtering 600 mL raw effluent. Membrane performance was evaluated in terms of permeate flux and water quality of the permeate. All experiments were performed in

random order and each filtration test was conducted in duplicate to ensure the reproducibility of the results (less than 3% variation was observed) and average values were reported.

3.8 *Membrane cleaning methods*

Membrane cleaning was performed by backwashing and/or ultrasonic cleaning as described below. The efficiency of cleaning was assessed by comparing flux recovery and surface analyses. The surface of cleaned membranes was examined by Fourier transform infrared (FTIR) spectrometry and scanning electronic microscopy which are detailed in section 3.9.

3.8.1 Backwashing

The fouled membrane was rinsed gently with Milli-Q water to remove particles on the surface, then turned over and backwashed by passing 150 mL of Milli-Q water through it at 70 kPa with a stirrer speed of 430 rpm. The cleaned membrane was then returned to the initial orientation and the flux recovery, $(J_w/J_0)\times100$, was determined after measuring the pure water flux (J_w) for the cleaned membrane. The flux recovery tests were conducted in duplicate and the observed variations were less than 3%.

3.8.2 Ultrasonic cleaning

Ultrasonic cleaning was performed by using a stainless steel basket submerged in a sonication bath (Sonica ETH3200, Soltec, Italy) filled with 4 L of Milli-Q water. The membrane was put in the middle of the basket with four pegs holding it in place, the fouled surface facing the bottom of the bath, the basket was placed in the same position within the bath for each run, and subjected to sonication. The initial water temperature was adjusted to 20°C. It was observed that the temperature increased to 26°C after 15 min sonication.

3.9 *Analytical methods and measurements*

This section contains the descriptions of the analytical methods and instruments using in this study. The physical and chemical characteristics of water samples were measured according to the Standard Methods for the Examination of Water and Wastewater (APHA, 1998).

Samples were filtered through 0.45 µm membrane (cellulose acetate, Advantec®, Toyo Roshi) before the analysis of dissolved organic carbon (DOC), ultraviolet (UV) absorbance, fluorescence spectra and Liquid Chromatography - Organic Carbon Detection (LC-OCD).

3.9.1 Turbidity

A turbidimeter 2100AN (Hach, USA) was used for the measurement of turbidity according to the manufacturer's instructions. It was calibrated regularly with StablCal turbidity standard calibration kit (Hach).

3.9.2 pH and conductivity

A SevenEasy pH meter (Mettler-Toledo) was used for measuring the solution pH. The calibration was performed regularly with buffer solutions at pH 4.0, 7.0 and 10.0.

The electrical conductivity of samples was measured with a SensION 156 portable multiparameter meter (Hach, USA). The instrument was calibrated using a KCl standard solution (0.01M). The temperature of samples was adjusted to 25°C before each measurement.

3.9.3 Dissolved organic carbon (DOC)

Dissolved organic carbon (DOC) was measured using a TOC analyser (Sievers 5310 C Laboratory, GE) which was equipped with an auto-sampler and an inorganic carbon remover (Sievers 900, GE) to reduce inorganic carbon levels in the sample. DOC

concentration was indirectly obtained by subtracting the two directly measured parameters: the total carbon (TC) and the inorganic carbon (IC).

3.9.4 Ultraviolet (UV) absorbance

Measurements of UV absorbance at 254 nm (UV_{254}) were conducted with a UV/vis spectrophotometer (UV2, Unicam). A pair of quartz cuvettes with 1 cm pathlength was used.

3.9.5 Specific UV absorbance

Specific UV absorbance (SUVA) (m^{-1} L mg^{-1}) was calculated as a ratio of the UV absorbance at 254 nm (cm^{-1}) to DOC (mg L^{-1}) multiplied by 100.

3.9.6 Fluorescence spectra

Fluorescence excitation emission matrix (EEM) spectra were determined using a PerkinElmer Fluorescence spectrometer (LS55). The wavelengths for emission and excitation were scanned in 5 nm increments from 200 to 550 nm and from 220 to 570 nm, respectively. The results were processed using FL WinLab software (PerkinElmer Applications).

3.9.7 Liquid Chromatography - Organic Carbon Detection (LC-OCD)

The molecular weight distribution of the organic components present in the effluent was determined using LC-OCD (LC-OCD Model 8, DOC-Labor Dr. Huber, Germany) at the Water Research Centre of the University of New South Wales, Australia. The LC-OCD Model 8 system consists of a HW-50S column (Toyopearl TSK, diameter 2 cm, length 25 cm) and an organic carbon detector which is equipped with a thin film reactor and non-dispersive IR-Detector. It separates the organic molecules on the basis of molecular size over the range 100–200,000 Da. Samples were diluted with Milli-Q water to adjust the dissolved organic concentration to the required range (1–5 mg L^{-1}). The chromatograms were processed using the Labview based program Fiffikus (DOC-Labor, Dr. Huber, Germany).

3.9.8 Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared (FTIR) spectroscopy was used to identify the components of fouling materials and to determine the degree of removal of the foulants after membrane cleaning using various methods. Membrane surfaces were analysed using a Spectrum 100 FT-IR spectrometer (Perkin Elmer, USA) with the attenuated total reflectance (ATR) method. FTIR spectra were measured over the wave number range of 650–4000 cm^{-1} at a scan speed of 0.2 cm sec^{-1}. The specimens were dried overnight in a desiccator before the analysis to ensure that the water peak did not interfere with the spectra.

3.9.9 Observation of membrane fouling layers

The surfaces of new, fouled and cleaned membranes were observed by environmental scanning electron microscopy (FEI Quanta 200) under wet mode (4°C, 5.8–5.9 Torr). The elements of the foulants deposited on the membrane were identified using an energy dispersive X-ray (EDX) detector attached to the microscope. The chamber was saturated with H_2O vapour and thus specimens remained moist during observation.

3.9.10 Particle size distribution

The size distribution of flocs from alum and ACH coagulation was determined using a Mastersizer X (Malvern Instruments, U.K.). The floc samples were collected from 5 cm below the surface of the solution using wide bore pipettes and inserted directly into the cell. There was a stirrer in the cell to distribute the particles during the measurement, however the floc diameters decreased with time. Therefore, the measurement was performed without stirring to minimise floc breakage. Before each measurement the cell was inclined 3 times to mix the sample gently to reduce floc agglomeration and sedimentation. Measurements were conducted in triplicate for each reading and five readings per sample were collected. Results were processed using Mastersizer software and plotted in volume percent within a particular size range.

Chapter 4. Ultrasonic membrane cleaning

4.1 *Preliminary experiment*

4.1.1 Power intensity of ultrasonic bath

A commonly used calorimetric method was employed to calculate the power intensity of the US transducer based on the change in the water temperature. The ultrasonic bath was filled with 5 litres of water and placed in a styrene foam box. The water temperature was recorded periodically over 15 min during ultrasonic irradiation (Figure 4-1).

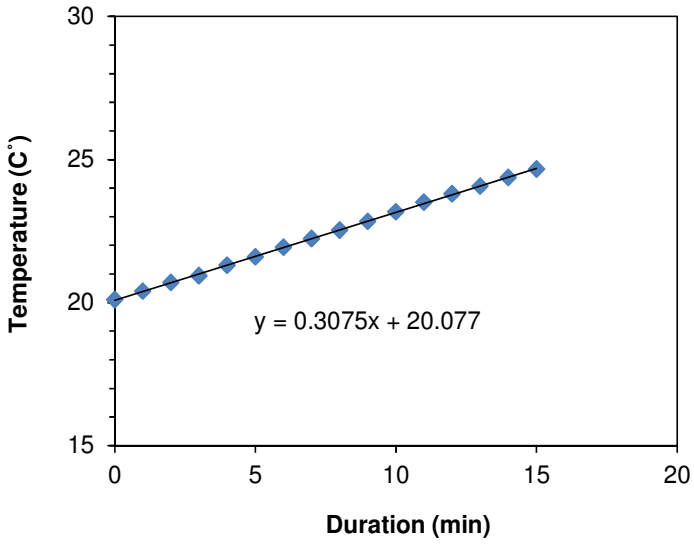


Figure 4-1 Temperature rise of water in the ultrasonic bath during ultrasound treatment

The average temperature increase per second (°C sec^{-1}) was substituted into Equation 4-1 to calculate the intensity:

$$\text{Power intensity (W)} = m_{water}\, C_{p\ water} \frac{\Delta T}{\Delta t} \qquad \text{Equation 4.1}$$

where

m_{water} is the mass of water exposed to sonication (g),

$C_{p\ water}$ is the specific heat capacity of water (g^{-1} °C),

$\Delta T/\Delta t$ is the average temperature change (°C sec^{-1}).

With the known specific heat capacity of water (4.18 J g^{-1} °C) and average temperature change (5.13 × 10^{-3} °C sec^{-1}), the output power intensity of the ultrasonic bath was calculated as 107 W.

4.1.2 Determination of backwashing method

Membrane fouling can be characterised as reversible or irreversible. Backwashing is a major cleaning method to remove membrane foulants. The volume of water necessary for membrane cleaning was determined by testing the flux recovery of two membranes fouled to different degrees: after filtration of 500 mL and 650 mL of the effluent sample (collection date: 30 Sep 2009). Regardless of the fouling degree, both tests demonstrated similar trends (Figure 4-2): the first 50 mL of backwashing gave a marked increase in flux recovery, which then levelled off gradually on reaching 150 mL. Flux recovery did not increase linearly with increasing volume of water used for backwashing and prolonged cleaning increased the water consumption rather than improving flux recovery. Therefore, the volume of water was set at 150 mL for backwashing and the flux recovery of this point could be considered as the cleaning efficiency of backwashing.

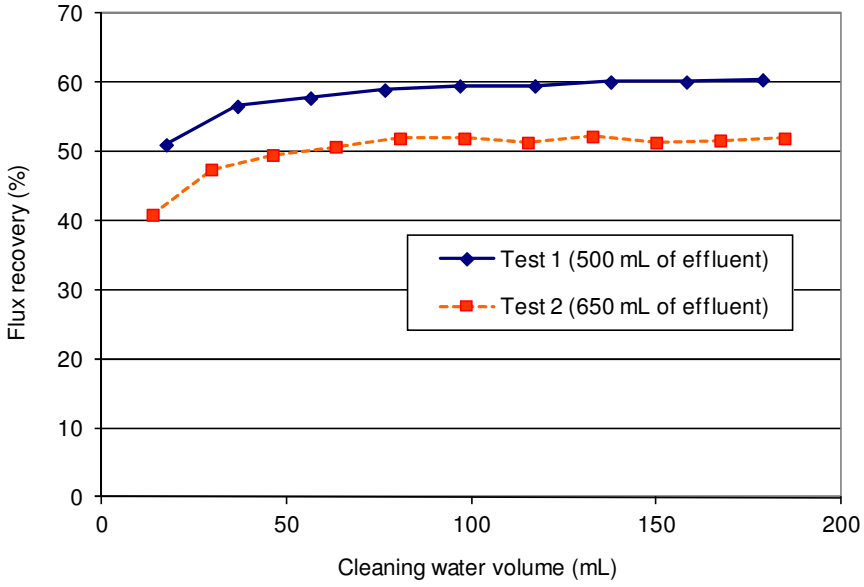


Figure 4-2 Cleaning efficiency related to volume of water used for backwashing

Test 1 and 2 represent backwashing after filtration of 500 and 650 mL effluent sample, respectively.

4.2 *Ultrasonic cleaning of membranes fouled with raw biologically treated effluent*

Ultrasonic cleaning of membranes fouled with 600 mL raw effluent (collection date: 16 Nov 2009) was conducted for 5, 10 and 15 min. Cleaning efficiency was evaluated as flux recovery. Figure 4-3 shows the flux recovery of the membranes after ultrasonic cleaning, backwashing using 150 mL Milli-Q water and the combination of US and backwashing. For sonication alone 10 min exposure gave maximum flux recovery with 85%, which was 10% higher than backwashing. Longer US cleaning (15 min) did not improve the cleaning efficiency. The combination of 10 min US and 150 mL backwashing was more effective than using these methods individually; US cleaning prior to backwashing was slightly more effective than vice versa. The cleaning efficiency was investigated by direct observation of the membrane surface using scanning electron microscopy.

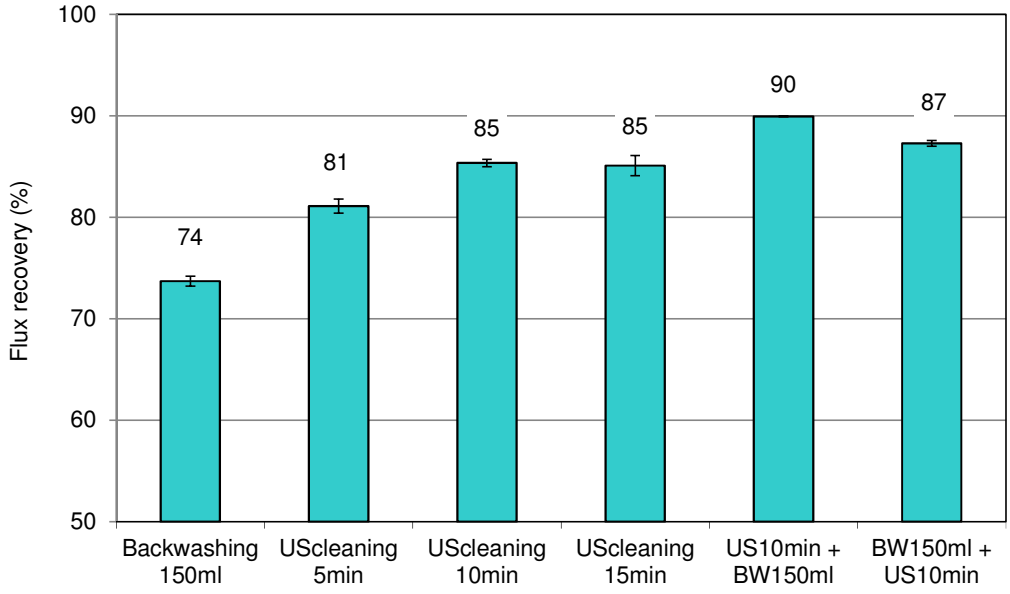
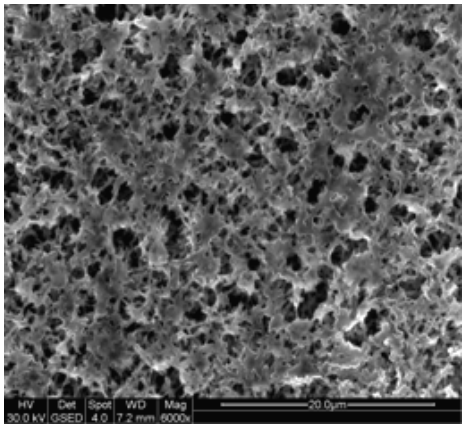
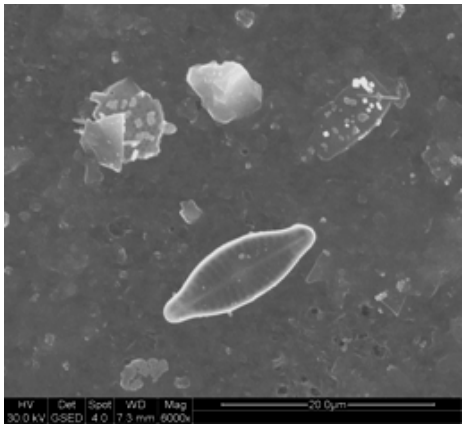


Figure 4-3 Flux recovery after backwashing (BW), US cleaning and combination of these

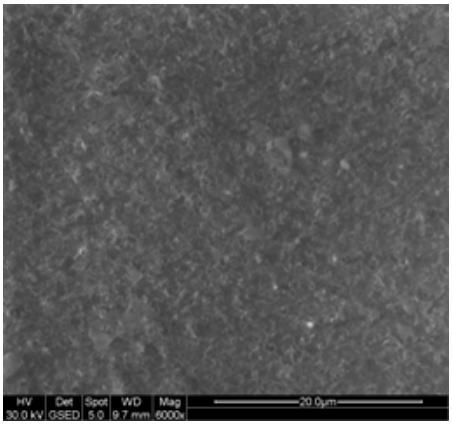
SEM images of the surfaces of a new membrane (a), a membrane fouled with the raw effluent (b) and membranes cleaned by backwashing (c), ultrasonication for 10 min (d) and a combination of the two methods (e) are shown in Figure 4-4. Compared to the new membrane, the surface fouled with raw effluent was covered with a jelly-like layer which contained particles, microorganisms and salt precipitates. Figure 4-4 (c) shows that the backwashing was not sufficient to remove the cake layer on the membrane surface as neither the membrane material nor pores can be seen clearly from the image. Ultrasonication (Figure 4-4d) was more effective than backwashing as it was able to detach the fouling layer from the membrane surface. US could loosen the internal fouling and open the membrane pores but pore clogging seems to partially remain. The ultrasonically generated turbulence was not capable of transporting the foulants from the membrane pores to the bulk solution. Although no significant difference was observed in the image of the cleaned surface using the combination of US and backwashing (Figure 4-4e) compared with the surface cleaned by US alone, the flux recovery was higher for the cleaning combination. It indicates that the combination of US and backwashing enhanced the removal of the internal membrane foulants. The improved cleaning efficiency was attributed to the acoustic streaming and/or the cavitation produced by US irradiation loosening the foulants on the membrane surface (Lamminen et al., 2004) followed by flushing the detached foulants from the pores and the surface of the membrane by backwashing.



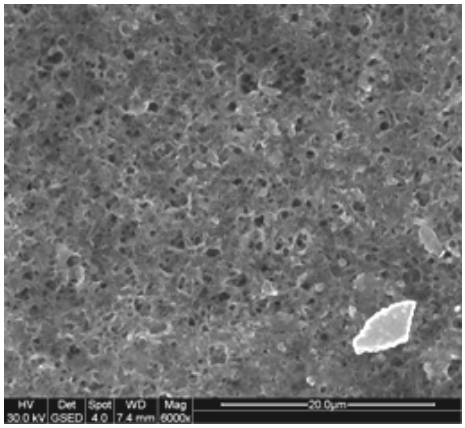
a. New PVDF membrane



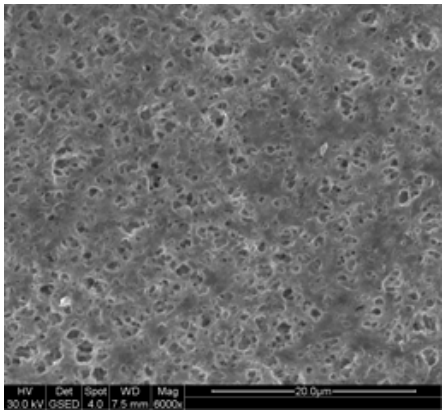
b. Fouled with raw effluent



c. After backwashing



d. After US cleaning 10 min



e. After US 10 min + BW

20.0 µm

Scale

Figure 4-4 SEM images of new, fouled and cleaned membranes (ESEM mode, Magnification x 6000, bar represents 20 µm)

ATR-FTIR has been commonly used for identification of chemical bonds or functional groups present in a sample. Each peak demonstrates a specific type of molecular vibration such as bending, rocking and twisting. For the assessment of membrane fouling and cleaning efficiency, this technique was adopted for characterisation of the chemical composition of foulants accumulated on the membrane. FTIR spectra of new membrane, the membrane fouled with the raw effluent and the membrane cleaned by backwashing or ultrasound (10 min) are shown in Figure 4-5.

Peak locations for the new membrane observed in this study and corresponding functional groups are listed in Table 4-1. The spectrum of the new membrane shows typical peaks for PVDF with strong absorbance at around 1214, 1183 and 873 cm^{-1} and medium absorbance at 1405, 1382, 1070 and 764 cm^{-1}, which were observed in the IR spectra of PVDF film in several publications (Kobayashi et al., 1975; Boccaccio et al., 2002; Benz and Euler, 2003). It should be noted that a very small peak at 1729 cm^{-1} indicates the presence of carbonyl C=O functions. It is introduced to the PVDF membrane in the process of hydrophilic modification and is not present in the original hydrophobic PVDF (Flösch et al., 1992; Singh et al., 2005).

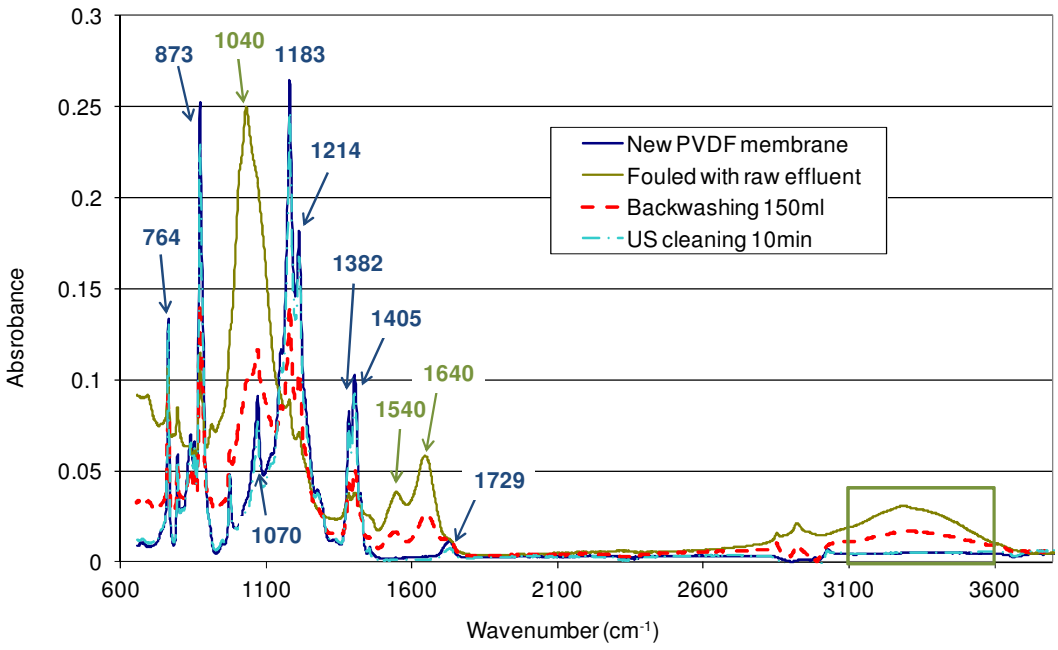


Figure 4-5 FTIR spectra of new PVDF membrane, the membrane fouled with the biologically treated effluent and membranes cleaned with backwashing and US cleaning

Table 4-1 Peak locations of new PVDF membrane and corresponding components

Wavenumber (cm^{-1})	Type of functional group
764	PVDF skeletal bending, CF_2 bending [4]
795	CH_2 rocking [4]
841	CH_2 rocking [4]
855	CH_2 rocking [1]
873	PVDF skeletal bending [1]
974	CH_2 twisting [1]
1070	CF-CF stretching [2]
1183	CH_2 bending, CH_2 wagging [1]
1214	CF_2 stretching, CH_2 wagging [1]
1382	CH_2 bending, CH_2 wagging [1]
1405	CH_2 wagging [2]
1729	Carbonyl group [3, 5]

[1] Kobayashi et al. (1975) Bachmann et al.(1979)

[3] Flösch et al. (1992)[4] Salimi and Yousefi (2003)

[5] Singh et al. (2005)

The major foulants for the raw effluent were compounds with peaks at wavenumbers 1040, 1540 and 1640 cm^{-1} and a wide peak in the range 3100-3600 cm^{-1}. The peak between 1000 and 1120 cm^{-1} and a broad band near 3400 cm^{-1} correspond to C-O stretching and OH functions, respectively, which indicate the presence of polysaccharide-like materials (Jarusutthirak, 2002). The peak for the C=O bond (1640 cm^{-1}) and N-H peaks at around 3300 and 1550 cm^{-1} suggest that amide bonds are present in the fouling layer, eg., as proteins (Nguyen et al., 2009). These polysaccharide-like and proteinaceous compounds (known as soluble microbial products: SMPs) are derived from the biological treatment process and are major problematic components for flux reduction of MF (Laabs et al., 2006).

The surface cleaned by backwashing shows traces of fouling components: peaks for polysaccharides and proteinaceous materials remained, whereas the spectrum of the

membrane cleaned by US almost matches that for the unused membrane. These results also confirm that US cleaning was more effective than hydraulic backwashing. However as the ATR-FTIR technique can evaluate only the surface of a specimen (i.e., penetration depth less than a few micron) (Boccaccio et al., 2002), these results do not indicate internal fouling of the membrane. So, although these FTIR results show almost complete removal of foulants by US treatment, the flux recovery data indicate that some internal fouling of the membrane remained.

4.3 *Cyclical cleaning of membrane fouled with raw effluent*

US cleaning was compared with backwashing in multiple cycles of microfiltration of the raw effluent (sample collection date: 09 March 2011). Filtration was performed at constant pressure (70 kPa) until the flux reached 35 L m^{-2} h^{-1}. The efficacy of cleaning was evaluated by comparing the flux recovery after membrane cleaning (Figure 4-6), the flux profile of the raw effluent in the five consecutive cycles with backwashing (Figure 4-7) and US cleaning (Figure 4-8), and the permeate volume (Figure 4-9).

For backwashing, flux recovery in the first run was 56% which dropped to 23% by the third run and then it stabilised at around 20% after the fourth cycle. During the cyclical operation, the accumulated effluent organic matter (EfOM) on the membrane surface and inner pores could not be detached. This was attributed to the residual foulant developing a strong affinity with the membrane materials and contaminants in the next filtration cycle. The foulant layer was also compacted under the pressurised condition and less was removed by hydraulic cleaning. A gradual reduction occurred for US cleaning over the five cycles, flux recovery decreasing from 84% to 64% in the final run. As mentioned for the SEM and FTIR analyses in the single cycle cleaning experiments (section 4.2), the cake layer was effectively removed by ultrasonic cleaning and the reduction in the flux recovery was mainly attributed to the adsorption of organic solutes to the walls of the membrane pores. Although the effluent sample used in this section showed relatively low specific UV absorbance (SUVA) and turbidity (1.59 L m^{-1} mg^{-1}, 1.2 NTU) compared with the sample in section 4.2, (2.29 L m^{-1} mg^{-1}, 3.1 NTU) and permeate volume was also different (650 mL cf. 600 mL), US cleaning produced a consistent cleaning efficiency in the first cycle (i.e., approximately 85%), whereas that

the flux recovery after hydraulic cleaning varied depending on the characteristics of the effluent and the load of the foulants (i.e., 74% in section 4.2 and 56% in this section).

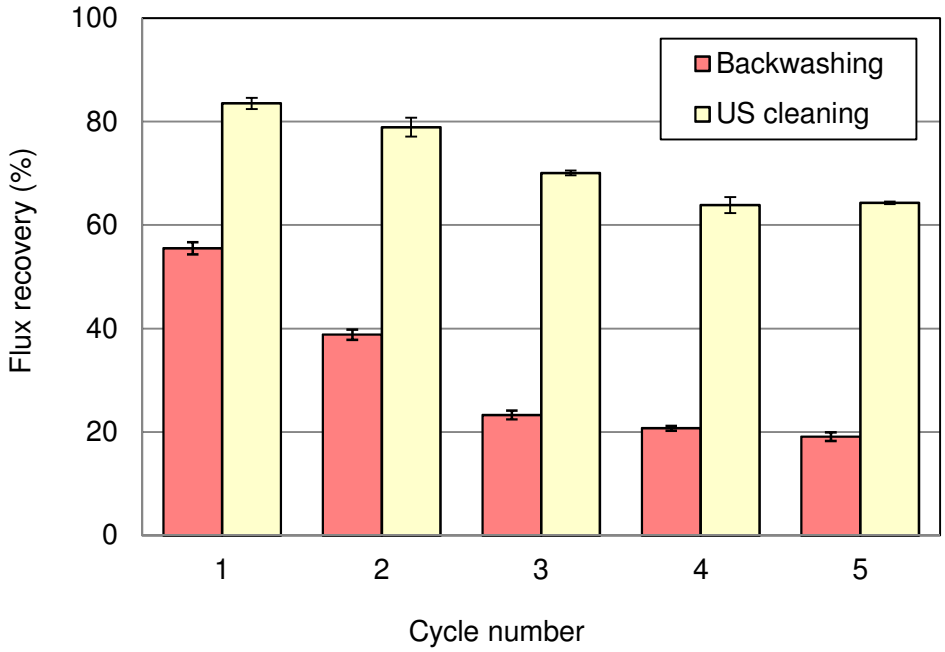


Figure 4-6 Flux recovery of 5 cycles of membrane cleaning with backwashing and ultrasonic cleaning

The permeate flux for 5 filtration cycles with backwashing and US cleaning is illustrated in Figures 4-7 and 4-8, respectively. The flux pattern in the first cycle shows a rapid initial drop until the permeate volume reached 200 L m^{-2}, followed by a gradual reduction. The initial section represents rapid pore blockage which generally occurs in the initial filtration stage and is followed by the accumulation of a cake layer (Song, 1998). The starting flux decreased dramatically with successive filtration cycles which was due to the poor cleaning efficiency of backwashing which was not sufficient to detach foulants from the membrane surface and pores. The remaining foulants within the membrane pores caused the rapid development of pore blockage, accompanying this, the transition of filtration stage occurred earlier.

Compared with backwashing, US cleaning maintained greater membrane performance over the multiple filtration cycles. Although the membrane flux was not fully restored

by US cleaning, it exhibited a long decline in each cycle, which indicated that the fouling started with pore clogging and transited to the cake layer accumulation.

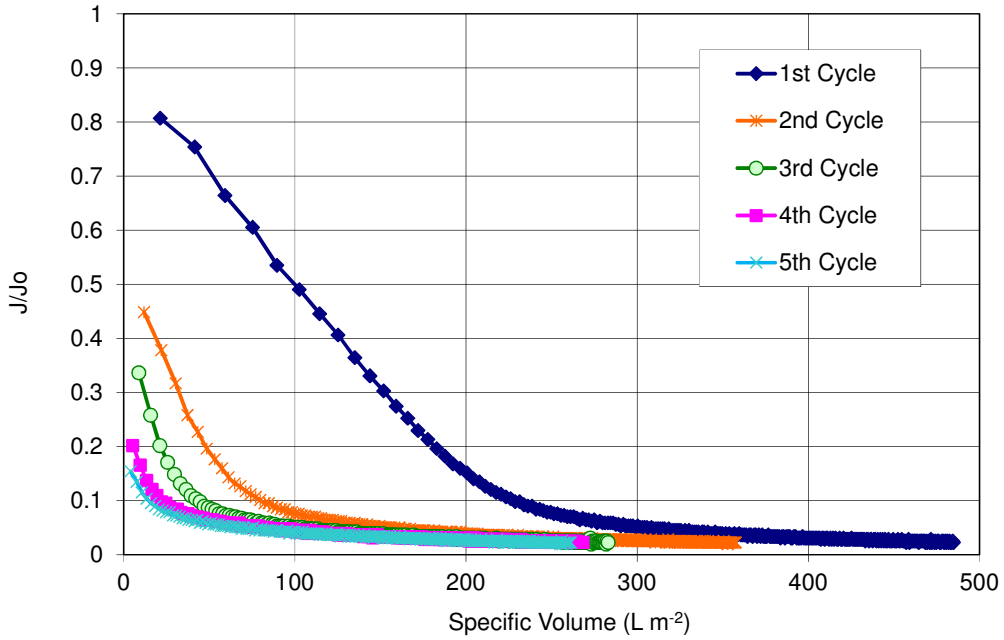


Figure 4-7 Normalized permeate flux for five cycles with backwashing

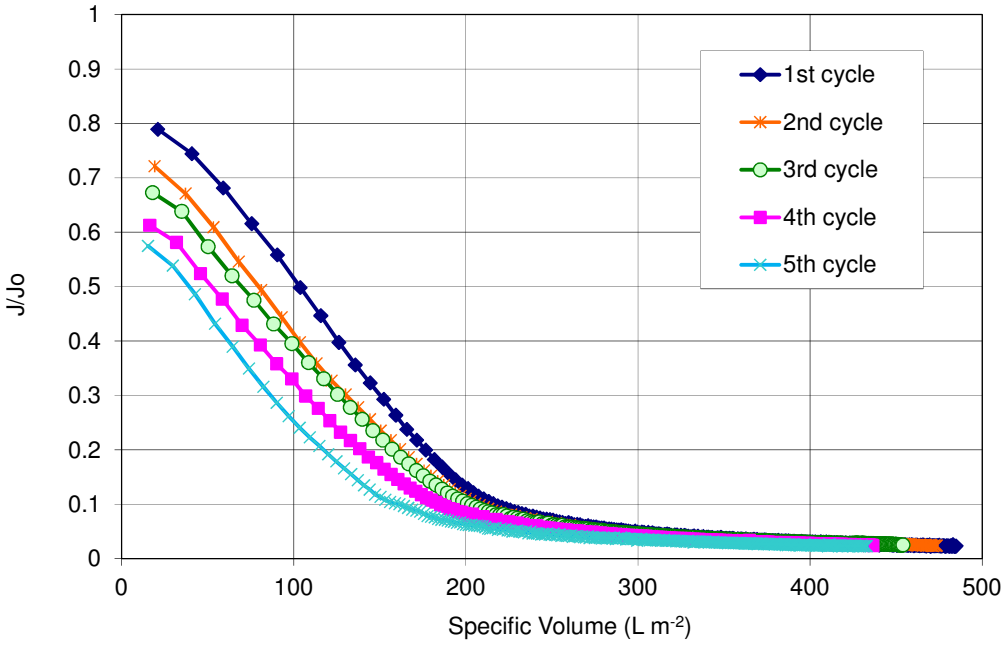


Figure 4-8 Normalized permeate flux for five cycles with US cleaning

Figure 4-9 shows the permeate volume for each cycle of filtration when the flux reached 35 L m^{-2} h^{-1} where backwashing and US were used for membrane cleaning. When

backwashing was used the permeate volume for the first run using the new membrane was 650 mL, then it underwent a severe reduction in the filterability in the second cycle. By the fifth cycle, it levelled off to about 350 mL. The dramatic reduction in filterability in the first few cycles was due to hydraulically irreversible fouling resulting from the strong affinity of the effluent organics with membrane materials. A gradual compression of residual foulants also contributed to the deterioration in the filterability. In contrast to this, there was little reduction in permeate volume when US cleaning was used, with a maximum of 8% reduction. Although considerable irreversible fouling occurred for US cleaning (i.e., 64% of flux recovery in the final cycle), filterability remained relatively stable. This may relate to the degree of compaction of the internal membrane fouling. As observed in the single cycle US cleaning, US could loosen foulants clogging membrane pores and thus the residual foulants might have less filtration resistance than for backwashing.

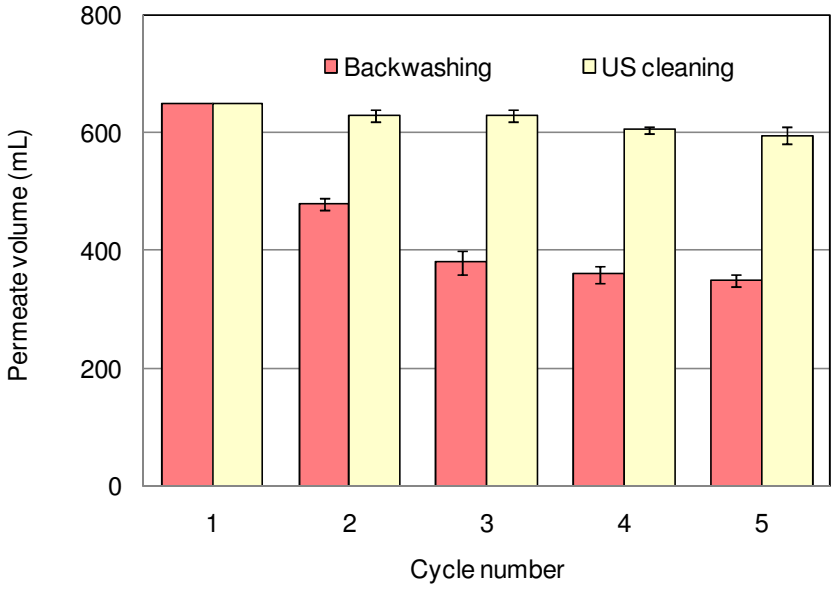


Figure 4-9 Permeate volume after cyclical cleaning with backwashing and ultrasonic cleaning

Although US cleaning effectively loosened and detached organic foulants from the membrane, some reports noted that US could damage polymeric membranes (Masselin et al., 2001; Lamminen et al., 2006). The impact of US on membrane structures was investigated by SEM, FTIR spectra of ultrasonically cleaned membrane after the 5 filtration-cleaning cycles, and measuring the permeate quality (DOC and UV_{254}). It was

possible that the gradual reduction in flux recovery during the cyclical US cleaning (observed in Figure 4-6) was due to modification of the membrane surface (i.e., change in hydrophilic property) caused by ultrasound, and this was assessed by the FTIR technique as described below.

The SEM images of membrane surfaces cleaned with US did not show any visible damage. In an aging study of PVDF membranes conducted by Puspitasari et al. (2010), FTIR spectra of hydrophilic PVDF membrane showed the elimination of the carbonyl peak (1729 cm^{-1}) after 4 cleaning cycles using sodium hypochlorite, which led to reduced hydrophilic characteristics of the membrane. The FTIR spectrum (Figure 4-10) of the membrane after cyclical US cleaning clearly showed the same peaks as the virgin PVDF membrane, including the peak for carbonyl groups. Therefore the hydrophilic characteristics of membrane remained after the multiple cleaning cycles.

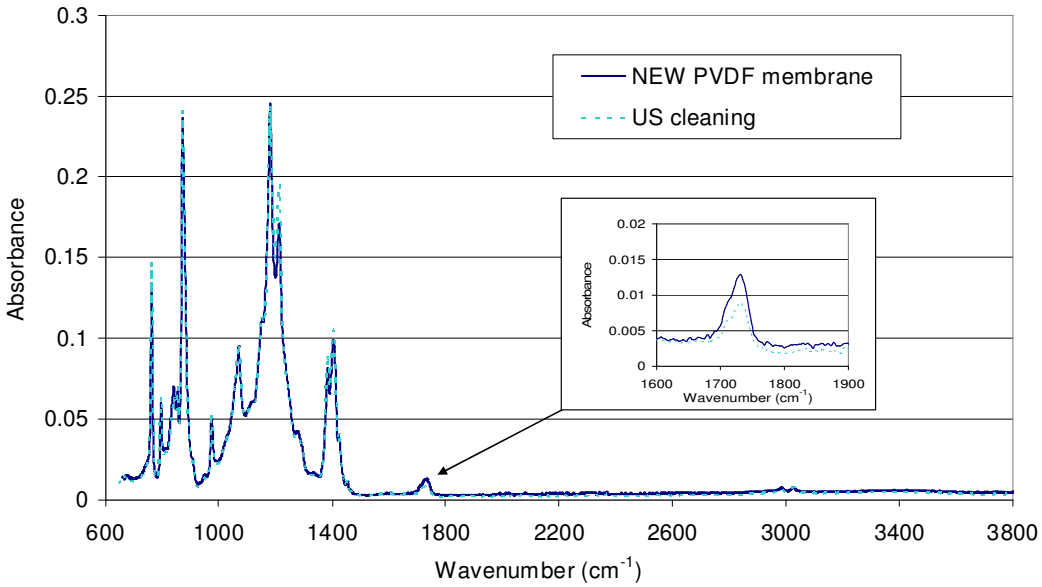


Figure 4-10 FTIR spectra of a virgin membrane and after 5 fouling and cleaning cycles

For both backwashing and US cleaning, the variation of DOC and UV_{254} for the MF permeate over the 5 cycles was less than 5% and 0.5%, respectively, which are within experimental error (Figure 4-11).

These results suggested that ultrasonic cleaning at 45 kHz and 107 W did not have negative impact on the membrane material over 5 cycles. However, the effects over many hundreds of cycles should be investigated as the membrane may be gradually degraded by US. As shown in other studies (Masselin et al., 2001; Lamminen et al., 2006; Sui et al., 2008), US at high intensity and continuous application could cause membrane damage due to its powerful mechanical force.

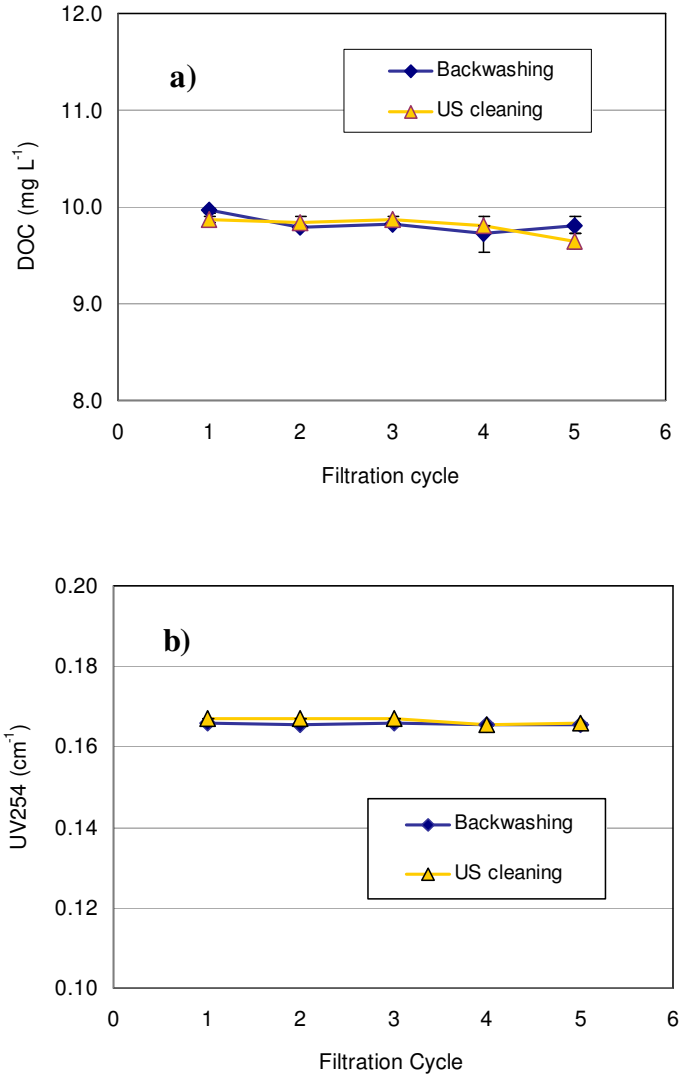


Figure 4-11 Permeate quality for each filtration cycle: (a) DOC and (b) UV absorbance at 254 nm

4.4 *Summary of findings for US membrane cleaning*

Ultrasonic cleaning (45 kHz, 107 W) of the MF membranes fouled with an activated sludge-lagoon wastewater effluent was investigated at lab-scale. US for greater than 5 min achieved higher flux recovery compared with backwashing. The combination of US with backwashing was more effective than using these methods individually, and US cleaning prior to backwashing was slightly more effective than vice versa. ATR-FTIR analysis showed that the components of the EfOM causing hydraulically irreversible fouling were protein-like and polysaccharide-like substances, and that US could dislodge them from the membrane surface. SEM images of membrane surfaces cleaned by US showed that US effectively detached the fouling layer from the surface as well as loosened the foulants blocking the membrane pores. As a result, the material blocking the pores was readily flushed away from the membrane pores when US was followed by backwashing.

The cleaning efficiency of US was significantly greater than backwashing in multiple effluent microfiltration cycles. The reduction in the permeate volume in the fifth cycle was less than 10% for US, whereas it nearly halved for backwashing. The quality of the product water remained consistent during the cyclical tests and there was no mechanical or chemical change in the membrane materials at the end of the fifth cycle. However, more work needs to be done to investigate the aging effect for long term operation.

Chapter 5. Feed pre-treatment by ultrasound

5.1 *Introduction*

This chapter details the study of the effects of ultrasound feed pre-treatment on the fouling potential of organic components present in the municipal wastewater effluent. The effect of US was evaluated in terms of MF performance including permeate flux and quality of the product water, flux recovery of fouled membranes and change in feed properties. The combination of US and Al^{3+}-based coagulation was also examined to investigate the impact of US on the changes in the floc characteristics on the performance of the coagulation treatment.

5.2 *Effect of ultrasonic feed pre-treatment on MF performance*

Microfiltration of the raw and ultrasonically treated effluent was conducted to investigate the effect of US on membrane performance. The effluent used in this experiment was collected on 30 September 2009. The permeate flux profile of the raw effluent shows a typical curve with an initial rapid decline followed by a slow flux reduction (Figure 5-1). Although the flux decline patterns of the US pre-treated effluent had a similar trend, there was an increasing initial flux decline with increasing duration of ultrasonic treatment of the feed water. The increased membrane filtration resistance was attributed to rapid pore blockage by the increasingly smaller particles resulting from extended US irradiation. Pore blocking generally proceeds quicker than the formation of cake layer and also has a greater impact on the flux decline (Lim and Bai, 2003). The particles with smaller size than the membrane pores can enter the pores and deposit on the pore walls, which leads to pore constriction. As suggested by Song (1998), when the particles and the membrane pores are similar in size, pore blocking becomes more significant. This is consistent with Bai and Leow's work (2002) which suggested that smaller particles cause much more severe fouling than larger particles for microfiltration.

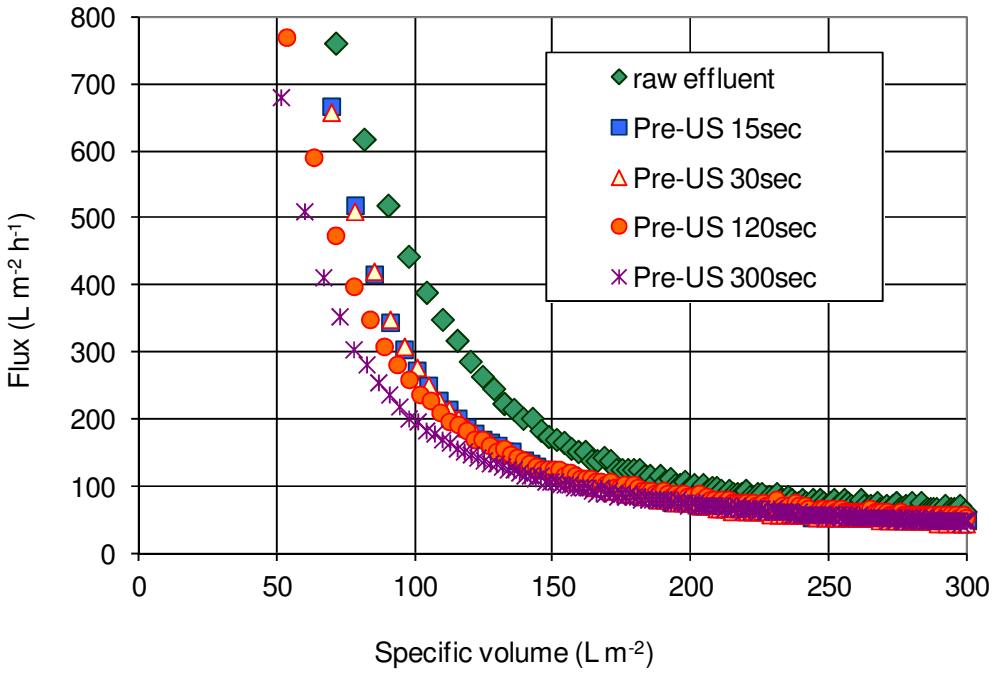


Figure 5-1 Comparison of permeate flux for MF of raw and US pre-treated effluent

To investigate the effect of the US feed pre-treatment on irreversible membrane fouling, backwashing was carried out on the membranes fouled with the raw and sonicated effluent. Irreversible fouling decreased significantly with increasing duration of US pre-treatment (Figure 5-2). The best flux recovery (~ 70%, 30% more than for raw effluent) was observed for 120 sec US treatment. The reduction in irreversible fouling could be explained by either or both of two possible mechanisms: (i) the more rapid pore blockage resulting from the increasingly smaller particles reduced the access of the organic solutes to the inner membrane pores for adsorption, and (ii) the irreversible fouling potential of the effluent organics was lowered due to the modification of their surface properties by US irradiation. However, prolonged sonication (300 sec) of the feed resulted in a small increase in irreversible fouling, this was likely due to the increasingly smaller particles becoming increasingly trapped within the membrane pore structures.

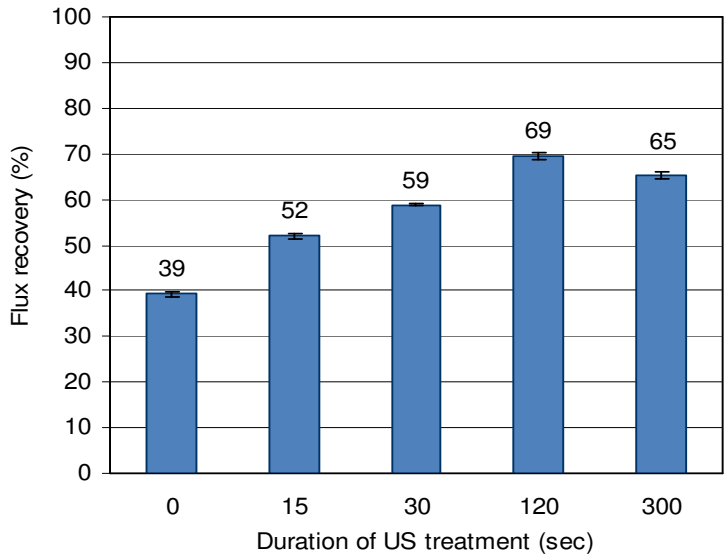


Figure 5-2 Flux recovery after backwashing of membranes fouled with raw and ultrasonically treated feed

5.3 *Effect of ultrasonic pre-treatment on the feed properties*

DOC, UV_{254} and turbidity were measured to identify the effect of ultrasonic irradiation on the feed properties. Although there were some fluctuations in all three for short term US irradiation, overall the values of these parameters increased with increasing US irradiation (Table 5-1). A significant increase in turbidity was observed. This was attributed to disintegration of the suspended solids to smaller fragments (Naddeo et al., 2007), which is consistent with the observation of increased initial fouling (Figure 5-1). The slight increase in the values of DOC and UV_{254} was attributed to the breakdown of particulates and colloidal organic substances into smaller organic components (ie., from non-dissolved to dissolved organics).

Table 5-1 Characteristics of raw effluent and the effluent treated ultrasonically for various durations

	DOC ($mg\ L^{-1}$)	UV_{254} (cm^{-1})	Turbidity (NTU)
Raw	10.1	0.164	4.8
After US pre-treatment			
15 sec sonication	9.9	0.160	5.2
30 sec	10.1	0.162	4.6
120 sec	10.7	0.170	6.1
300 sec	10.5	0.167	7.0

Figure 5-3 shows the fluorescence EEMs of the raw and sonicated effluent. The EEM spectra were divided into five regions according to Chen et al. (2003). Regions I and II correspond to aromatic proteins and region III is associated with fulvic acid-like substances. Region IV and region V are associated with soluble microbial by-products (SMPs, eg., proteins and polysaccharide-like materials) and humic acid-like materials, respectively.

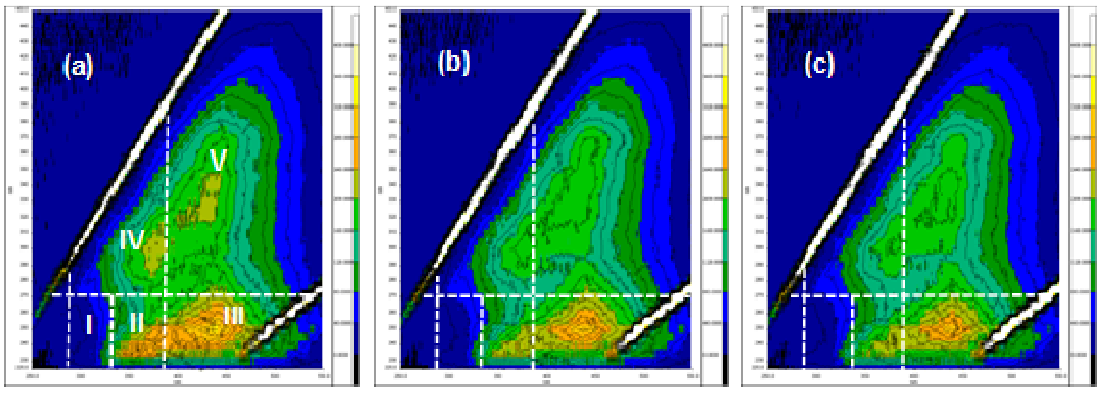


Figure 5-3 EEMs of the (a) raw effluent and the sonicated effluent after (b) 120 sec US pre-treatment and after (c) 300 sec US pre-treatment

Regions (I) and (II): aromatic proteins, (III): fulvic acid-like materials, (IV): SMPs and (V): humic acid-like materials

The peak intensity of aromatic proteins (II), SMPs (IV) and humic acid-like materials (V) decreased with increasing duration of US treatment, whereas there were only

marginal changes in the other peaks. Quantification of EEM intensity in each region was undertaken using fluorescence regional integration (Chen et al., 2003). After 300 sec sonication the spectra volumes of regions I, II, III, IV and V decreased by 7, 20, 11, 15 and 7%, respectively (Figure 5-4), indicating that aromatic proteins and SMPs were relatively more susceptible to US than humics.

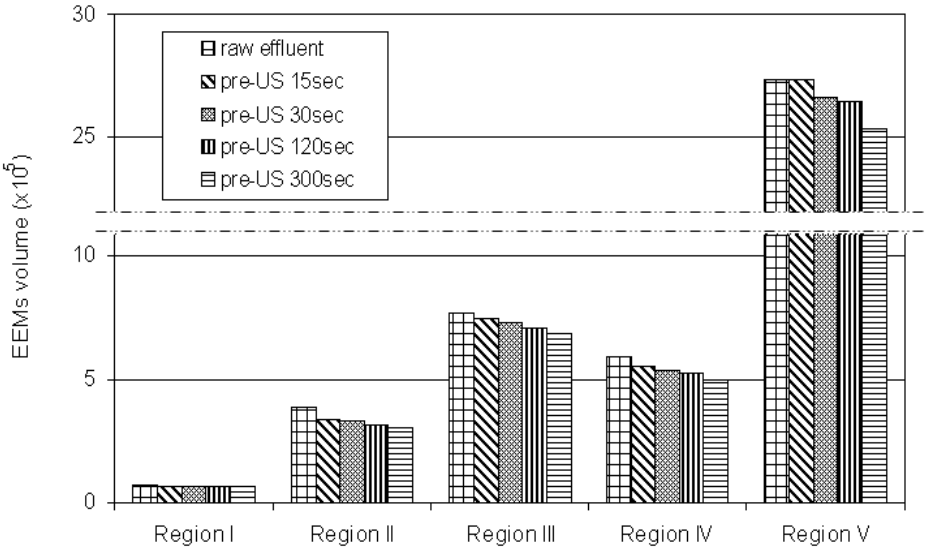


Figure 5-4 EEM volumes of the raw and effluent treated for various US durations

Identification of the membrane foulants was conducted by analysing the membrane surface using ATR-FTIR (Figure 5-5). The spectra of the virgin membrane and membrane fouled with the raw effluent were identical to those in Figure 4-5 and the peaks and corresponding functional groups are shown in section 4.2. The peak locations and appearance of the membrane foulants for the raw and sonicated (300 sec) effluent samples were very similar, but a significant reduction in the peak intensity of protein-like materials was observed for the foulant layer for the sonicated effluent. This indicates that US influenced the protein structures, consistent with the peak reductions for aromatic proteins and SMPs in the EEMs (Figures 5-3 and 5-4). In addition, the peaks for polysaccharide-like materials were slightly reduced compared with raw effluent. Some studies showed that US could alter the structure and functionality of organic components (eg., proteins and polysaccharides) (Gülseren et al., 2007; Yang et al., 2008). The structure/conformation and nature of proteins is determined by the

balance between various noncovalent interactions such as hydrogen bonding and hydrophobic and ionic interactions, which can be disrupted by ultrasonically induced shear forces (Stathopulos et al., 2004). Several reports suggested that the alterations in tertiary structure of proteins caused by US resulted in changes in their polymer characteristics (e.g., viscosity, solubility, gel formation, surface activity and intermolecular interactions) (Stathopulos et al., 2004; Güzey et al., 2006; Jambrak et al., 2008; Ashokkumar et al., 2009). It is therefore suggested that US modified the structures of the biopolymers, particularly the proteinaceous materials, which led to the reduced affinity of these compounds for the membranes.

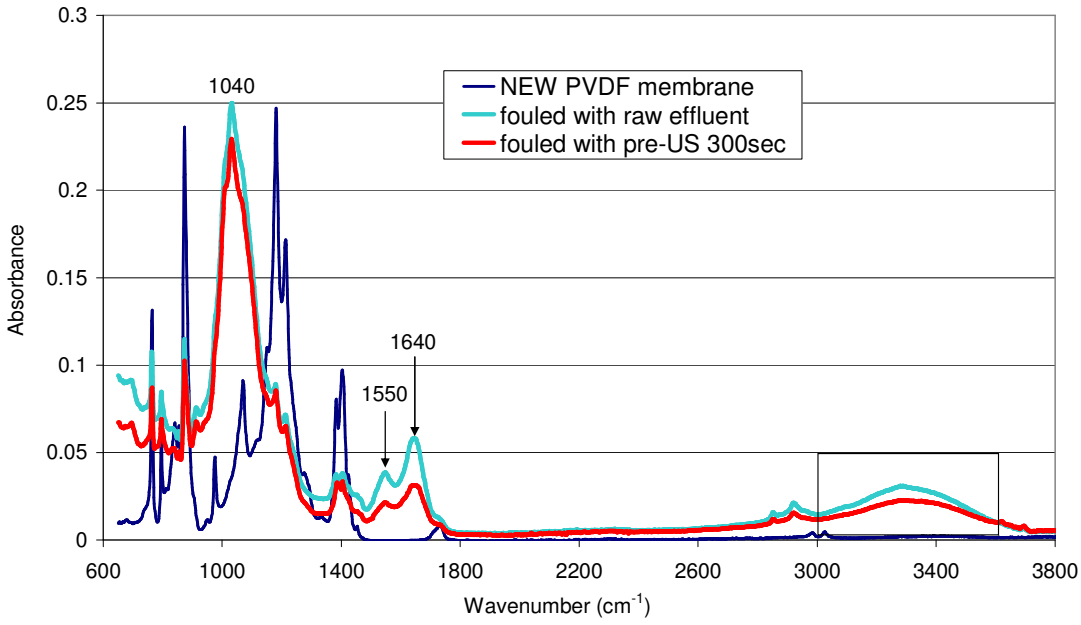


Figure 5-5 FTIR spectra of a virgin membrane and membranes fouled with raw and sonicated effluent

5.4 *Effect of ultrasonic feed treatment before coagulation on MF performance*

The flux for raw effluent (collection date: 06 May 2010), effluent pre-treated by coagulation using Al^{3+}-based coagulants (ACH and alum) and by US prior to Al^{3+}-based coagulation is shown in Figure 5-6. Optimisation of coagulant dose for the biologically treated effluent from the same water source was determined elsewhere (Fan et al., 2008;

Goh et al., 2010). Since the characteristics of the effluent sample in this study were very similar to those samples, and similar DOC removal and effective turbidity removal as well as good MF performance with nearly full flux recovery were observed, the coagulant dosage (5 mg L^{-1}) used by those researchers was used. Coagulation with both ACH and alum led to a dramatic increase in permeate flux, with the flux for alum being marginally higher than for ACH. US pre-treatment followed by coagulation gave a further increase in the permeate flux. This is consistent with a report in which improvement of flux was observed in the microfiltration of a surface water using US-alum pre-treatment with 240 sec US (Tran et al., 2007). The flux performance after alum and ACH coagulation was similar after 300 sec US, whereas after 120 sec US the performance for alum was a little better than for ACH. The small improvement in flux for the longer US time and so increased energy input (4.6 cf. 1.84 kWh m^{-3}) shows that optimisation of the system would be necessary to trade-off energy input and flux improvement.

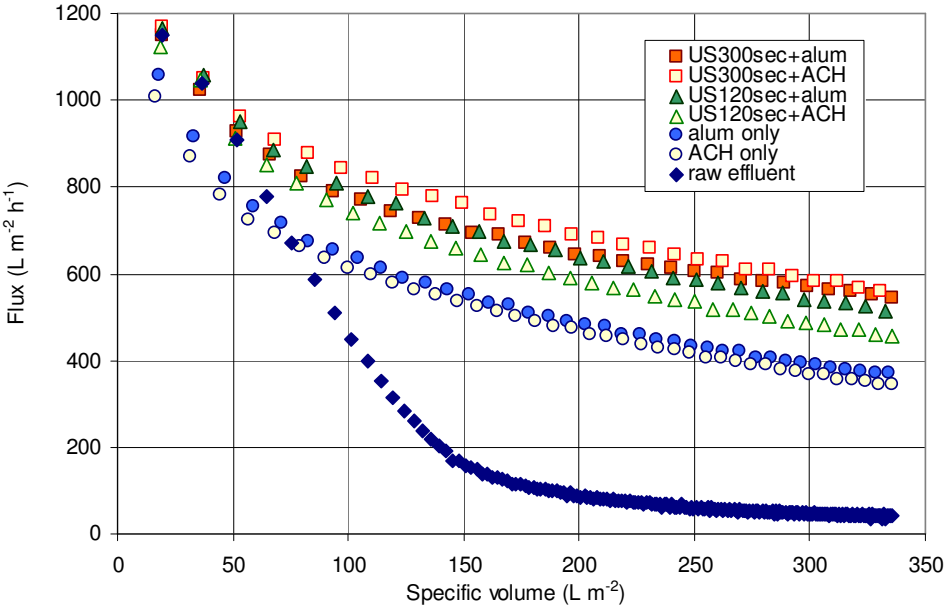


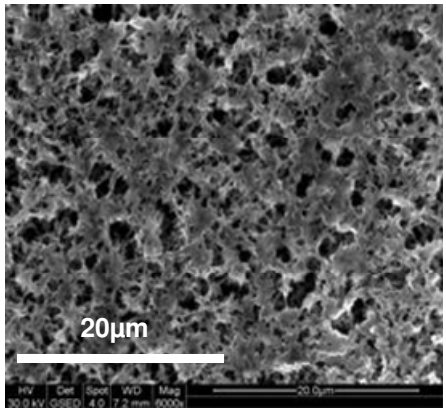
Figure 5-6 Permeate flux for MF of raw and effluent pre-treated by Al^{3+}-based coagulation or combination of US and coagulation

As demonstrated in the EEMs and FTIR analyses, the structures of the SMPs and proteins in the effluent were modified by US treatment, and these changes may have influenced the structure of the flocs. The fragmentation of particles within the effluent may also have played an important role in the formation of the flocs by creating more

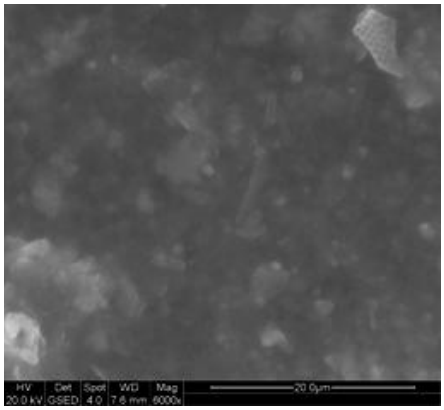
nuclei for floc development (Gregor et al., 1997). It is therefore suggested that the alteration in the physico-chemical properties of the effluent organic matter enhanced the interaction between the particulates and/or the organic solutes and the Al^{3+}. As a result, the permeate flux was improved due to the formation of a cake layer of lower resistance on the membrane surface. The different improvement in filtration resistance for alum and ACH may be attributed to the structurally different Al precipitates produced when alum and ACH were added to the feed (Wang et al., 2008). Flux recovery after coagulation with alum and ACH was 95%, compared with approximately 55% for the raw effluent, and the coupling of US and coagulation gave a flux recovery of more than 97% for both coagulants.

5.4.1 Observation of fouling layer

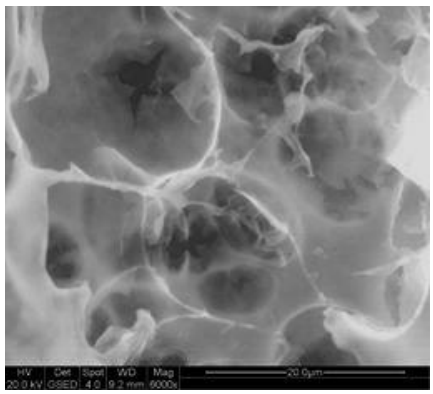
The fouling layers on the MF membranes for the coagulated effluent with and without US pre-treatment were examined using ESEM (Figure 5-7). The ESEM images of a virgin PVDF membrane and a surface fouled with raw effluent (Figures 5-7a and 5-7b, respectively) are provided for comparison. After MF of the untreated effluent, a dense and gel-like layer was formed on the membrane (Figure 5-7b). Fouling layers for ultrasonically treated and then coagulated samples (Figures 5-7d and 5-7f) exhibit a different morphology from the coagulated samples without US (Figures 5-7c and 5-7e). The floc layer for the US-ACH treated effluent appears to be rougher, being more porous and so providing more access to membrane pores compared with the coagulated effluent without US pre-treatment. Similar results were obtained for the alum treatment with and without US pre-treatment. It seems that the cake layer of the coagulated feed with US pre-treatment compacted less than the coagulated effluent without US pre-treatment, which resulted in an improvement in the permeate flux.



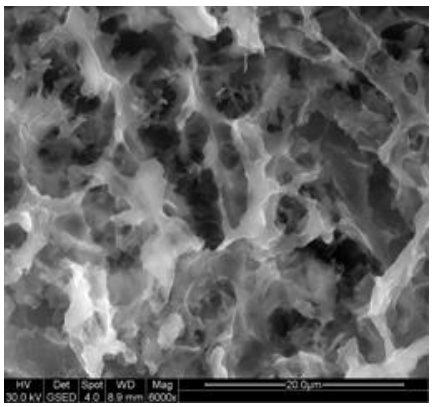
a. New PVDF membrane (Pore size 0.1 µm)



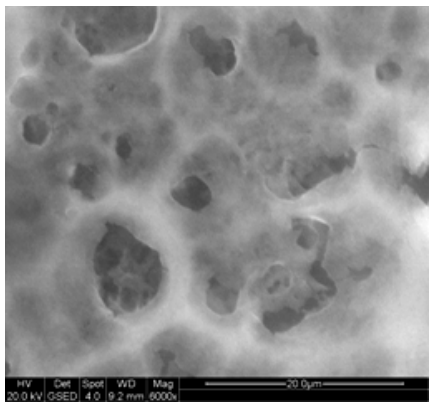
b. Fouled surface with raw effluent



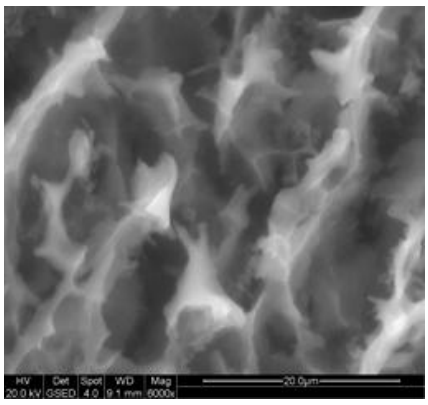
c. ACH only



d. pre-US 2 min + ACH



e. alum only



f. pre-US 2 min + alum

Figure 5-7 ESEM images (x 6000) of the surface of a new PVDF membrane and the surfaces of the fouled membranes for the coagulated effluent with and without US pre-treatment (bar represents 20 µm)

5.4.2 Effect on removal of effluent organic matter

The DOC of the raw and coagulated effluent with and without US pre-treatment was characterised using size exclusion chromatography (Figure 5-8). A LC-OCD chromatogram of the raw effluent is composed of five major fractions: (1) biopolymers (e.g., polysaccharides, proteins and amino sugars), (2) humic substances, (3) building blocks, (4) low-molecular-weight organic acids and (5) low-molecular-weight neutrals. Coagulation using ACH and alum (Figure 5-8a) showed similar results with a reduction in the biopolymers and large molecular weight humic substances, which indicates ACH and alum preferentially removed larger molecular weight components. This is consistent with the results obtained by Haberkamp et al. (2007) who conducted coagulation using aluminium chloride ($AlCl_3$) for a biologically treated secondary effluent. There was no significant difference for each fraction of the coagulated effluent whether US pre-treated or not.

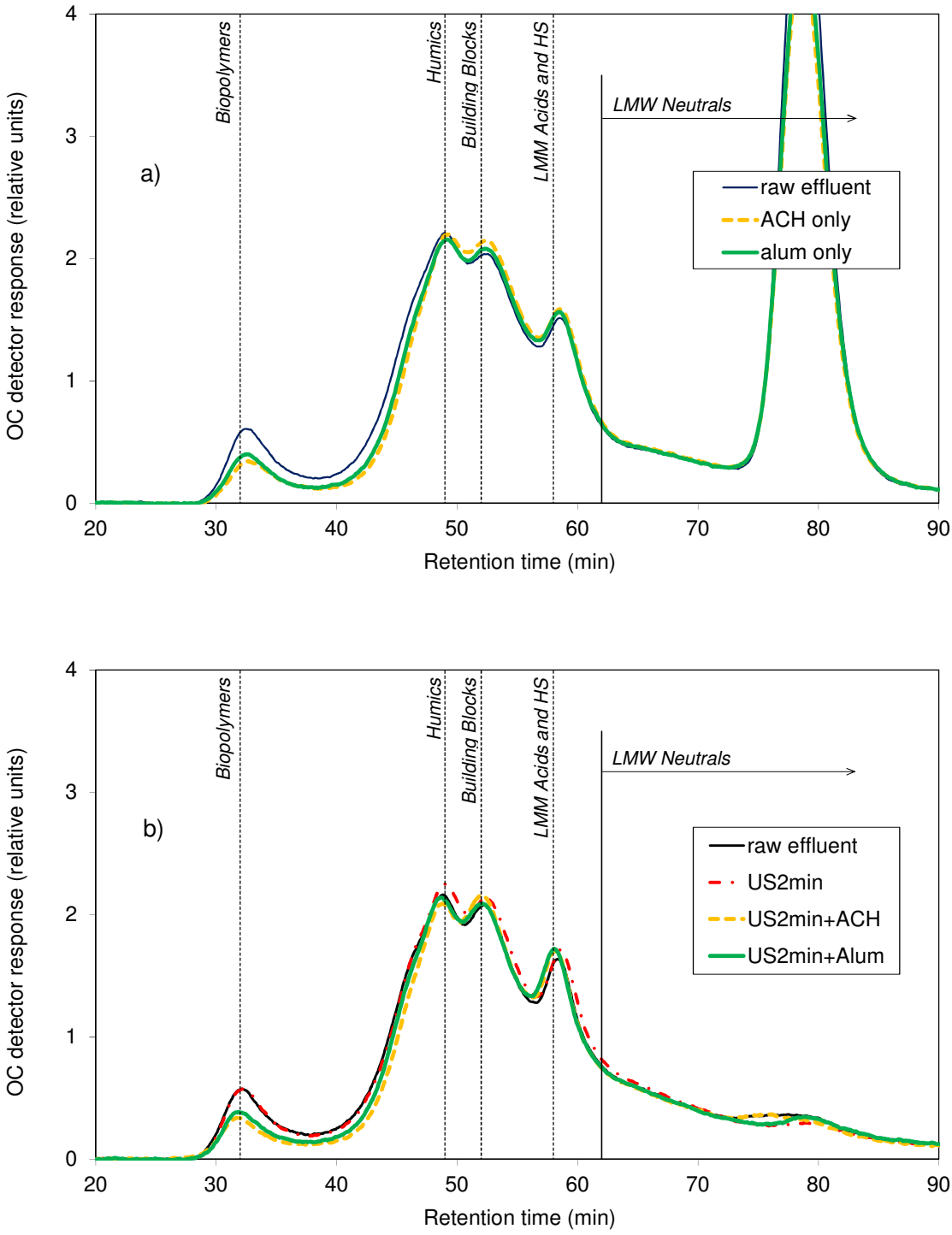


Figure 5-8 Molecular size distribution of effluent treated by a) ACH or alum coagulants and b) US prior to ACH or alum coagulation (each sample diluted threefold)

The effluent quality was examined to identify the effect of US on the removal of the contaminants after coagulation and MF (Table 5-2). Coagulation using ACH led to the removal of DOC and UV absorbance being approximately 5% and 4% higher, respectively, compared with alum. The better organic removal for the prehydrolysed aluminium coagulant (i.e., ACH) was attributed to the presence of a high concentration of Al_{13} species which have higher positive charges than monomeric Al as reported by Matilainen et al. (2010). After coagulation SUVA showed negligible change for both ACH and alum, which indicates removal of a similar ratio of aromatic to non-aromatic compounds by the coagulants. This result differs from general trends in which UV-absorbing compounds are more easily removed by coagulation using hydrolysed metal salts, as the SUVA of the solutions is often decreased after coagulation (Bratby, 2006; Howe and Clark, 2006). This was due to a difference in pH conditions, where coagulation was performed without pH adjustment (pH 7.9) in this study, whereas coagulation targeting the removal of NOM (i.e., treatment for surface water) often operates at pH between 6 and 7 due to the better removal of humic substances under slightly acidic pH conditions (Bratby, 2006). At this lower pH range alum can remove dissolved organics effectively and humic substances are preferentially removed. However, polysaccharides were observed to be resistant to removal by alum coagulation in a pH range of 5–7 (Chow et al., 2009) and thus SUVA may be significantly decreased. On the other hand, it is suggested that Al^{3+}-based coagulation in this study (at pH 7.9) removed larger molecular weight components, such as SMPs, including both aromatic compounds (e.g., proteins) and non-aromatic compounds (e.g., polysaccharides), as a result the SUVA did not change markedly.

The better quality of the MF permeate for the pre-treated effluent after using ACH compared with alum suggests that ACH removed slightly more effluent organics of smaller size which were not able to be retained by MF (e.g., humic substances). The other possibility is that the organic solutes had a lower adsorption potential for the membrane materials due to modification of their characteristics caused by adding alum.

Regardless of whether US treatment of the feed was applied or not, consistent performance was observed for both coagulants; the residual DOC and UV_{254} were fairly constant (Table 5-2) and no significant difference was observed in the EEM spectra for

each region (Appendix A). The modification of the surface properties of the dissolved organics seemed to have a marginal influence on coagulation performance and the product quality after MF.

Table 5-2 Characteristics of effluent before and after various treatments

	DOC		UV_{254}		SUVA	Turbidity
	(mg L^{-1})	Removal (%)	(cm^{-1})	Reduction (%)	(L m^{-1} mg^{-1})	(NTU)
Raw effluent	10.5	-	0.250	-	2.38	3.6
After pre-treatment						
ACH only	9.0	14.3	0.216	13.6	2.40	
US 30 sec + ACH	9.0	14.3	0.215	14.0	2.39	n.m.
US 2 min + ACH	9.0	14.3	0.215	14.0	2.39	
US 5 min + ACH	8.9	15.2	0.214	14.4	2.40	
alum only	9.4	10.5	0.226	9.6	2.40	
US 30 sec + alum	9.4	10.5	0.225	10.0	2.39	n.m.
US 2min + alum	9.3	11.4	0.226	9.6	2.43	
US 5min + alum	9.3	11.4	0.225	10.0	2.42	
MF permeate						
ACH only	8.7	17.1	0.214	14.4	2.46	
US 30 sec + ACH	8.6	18.1	0.213	14.8	2.48	< 0.1
US 2 min + ACH	8.7	17.1	0.214	14.4	2.46	
US 5 min + ACH	8.7	17.1	0.213	14.8	2.45	
alum only	9.0	14.3	0.219	12.4	2.43	
US 30 sec + alum	9.0	14.3	0.218	12.8	2.42	< 0.1
US 2min + alum	8.9	15.2	0.218	12.8	2.45	
US 5min + alum	8.9	15.2	0.218	12.8	2.45	

n.m.: not measured

5.5 *Effect of turbidity on the ultrasonically assisted coagulation*

The flux profiles of variously pre-treated effluent are shown in Figure 5-9 to Figure 5-11. Microfiltration performance was examined for the effluent with a turbidity of 1.0, 3.6 and 8.0 NTU (sample collection date: 11 May 2011, turbidity modified as described in section 3.1). More drastic initial decline in permeate flux resulted with increasing feed turbidity. Pre-treatment using alum or ACH led to an improved MF performance for the effluent over the range of turbidity. The particulates and colloids present in the raw effluent formed flocs with less filtration resistance. For coagulation alone, the lower the effluent turbidity, the better the filtration performance.

The effectiveness of US in increasing flux was greatly influenced by feed water turbidity. Since particle and colloidal matter can act as nuclei for floc formation at the beginning of the flocculation process (Gregor et al., 1997; Yan et al., 2008), the interactions between Al hydrate species and the particulates and colloids were thus more significant for higher turbidity samples due to the more frequent collision between the Al and particles.

Lee et al. (2000) explained that the different compressibility of flocs formed via sweep flocculation and charge neutralisation is due to the different water content within the flocs. Flocs formed by the sweep-floc mechanism are made up mostly of alum hydroxide precipitates which are gelated and contain a large amount of water. The sludge from sweep-flocs was found to be difficult to dewater (Thompson and Paulson, 1998). By contrast, the formation of flocs under charge neutralisation conditions involves a complex mixture of Al species, particulate and colloidal organics, as well as dissolved organic substances, thus the flocs are less compressible (Lee et al., 2000).

Although the coagulation conducted in this experiment was under sweep-floc conditions, the fragmented particles and colloids and organic solutes with modified surface properties, caused by US, may have interacted with the Al species due to the enhanced collision frequency and increased nuclei for floc formation. Therefore it is suggested that US feed pre-treatment may have induced the formation of less compressible flocs which might have led to the production of a spongy cake layer as illustrated in the

ESEM pictures of fouled membranes (section 5.4.1). The effect may be more significant in the presence of relatively high turbidity water.

For effluent turbidity of 3.6 and 8.0 NTU the flux for alum- and ACH-treated effluent was very similar (Figure 5-10 and Figure 5-11), whereas for the turbidity of 1.0 NTU the flux after alum treatment was considerably lower than for ACH (Figure 5-9). This may have been due to the lack of nuclei for alum and the limited number of collisions and contact opportunities at the low turbidity, unlike for ACH which contains polymerised Al species which allow the flocs to develop (Jiang, 2001).

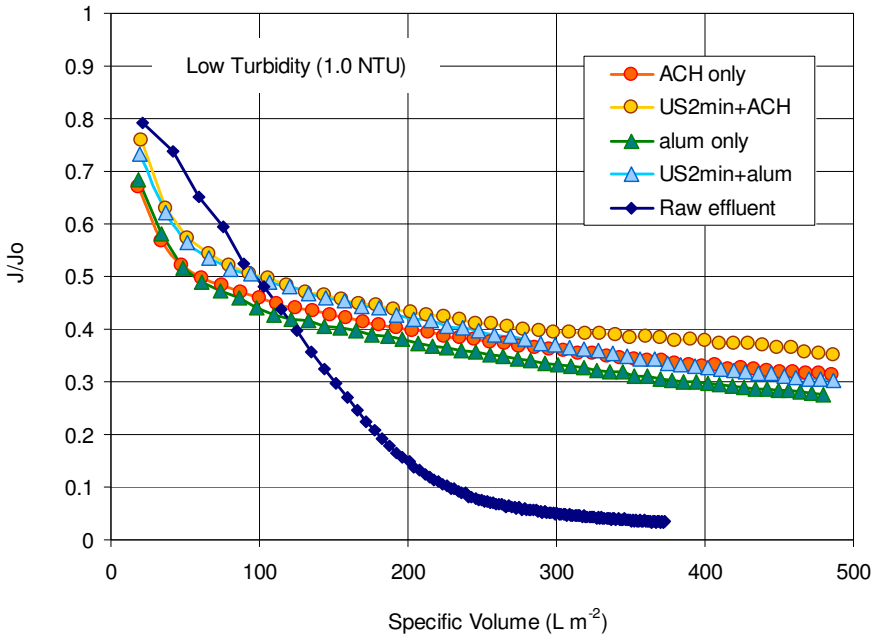


Figure 5-9 Flux pattern of raw effluent at initial turbidity of 1.0 NTU and effluent pre-treated with alum and ACH coagulants with and without US

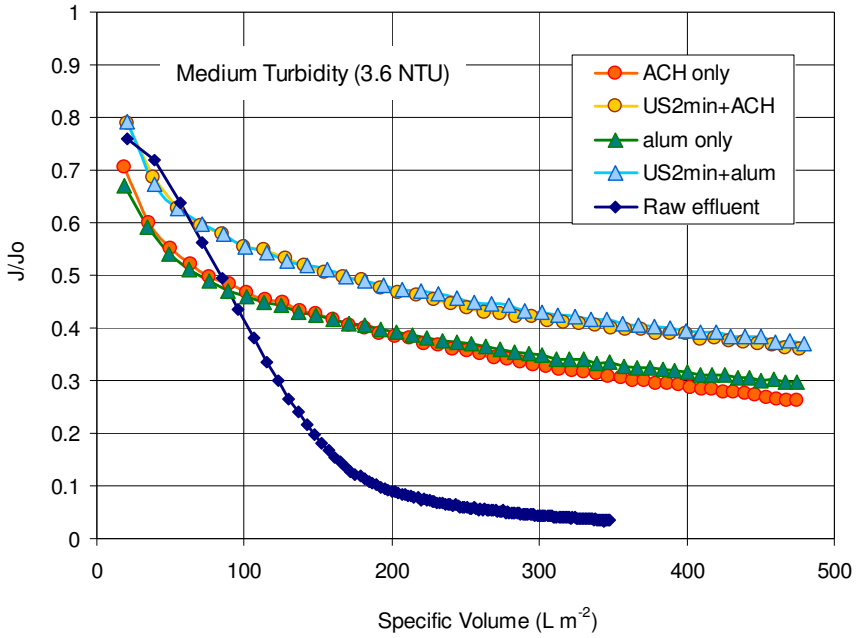


Figure 5-10 Flux pattern of raw effluent at initial turbidity of 3.6 NTU and effluent pre-treated with alum and ACH coagulants with and without US

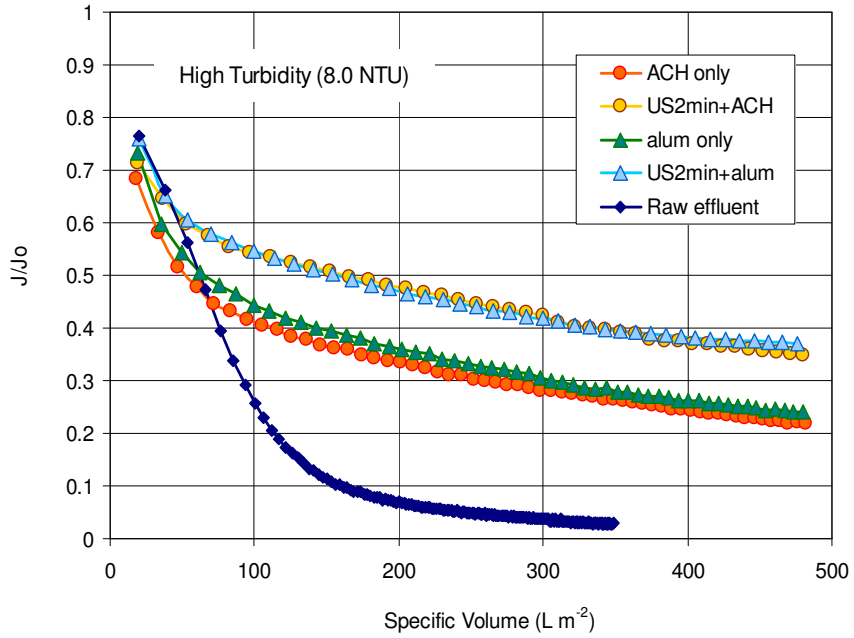


Figure 5-11 Flux pattern of raw effluent at initial turbidity of 8.0 NTU and effluent pre-treated with alum and ACH coagulants with and without US

The effect of initial feed turbidity on removal of dissolved organics by alum coagulation was investigated by comparing LC-OCD chromatograms (Figure 5-12). When the effluent was exposed to US for 2 min, the amount of biopolymers was significantly increased which was attributed to the fragmentation of the particulates and colloids. The removal of biopolymer by alum coagulation was higher for the effluent at initial turbidity of 3.6 NTU (removal: 60% for alum, 65% for US-alum) compared with for 8.0 NTU (removal: 23% for alum, 55% for US-alum). The lower organic removal for the higher turbidity sample may have been due to the reduced number of adsorption sites available on the Al precipitates or the overall negative charge of Al hydrolysis species due to the large amount of entrapped particulates.

The chromatograms for the coagulated effluent with and without US pre-treatment were identical for each fraction at turbidity 3.6 and 8.0. This suggested that the US pre-treatment improved the performance of MF by modifying the cake morphology without influencing the coagulation performance in terms of removal of dissolved organic matter.

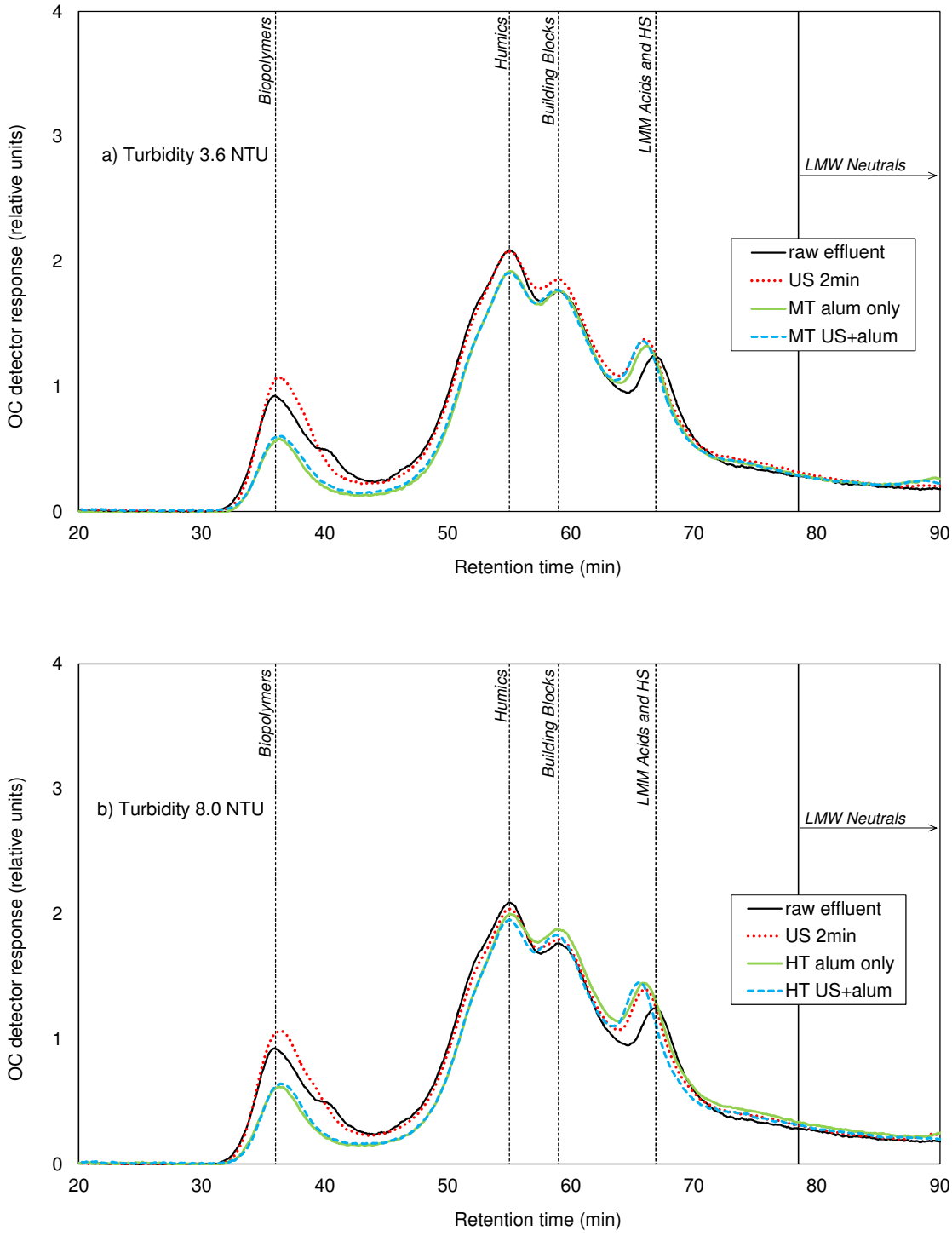


Figure 5-12 Molecular size distribution of effluent treated by alum coagulants with and without US pre-treatment for initial feed turbidity at a) 3.6 and b) 8.0 (each sample diluted threefold)

5.5.1 Particle size analysis

The different MF flux performance for the US-coagulation and coagulation only treated effluent was attributed to the different morphological structures of the resultant cake layers (section 5.4.1), which would be dependent on the physical properties of the flocs, such as size, shape/structure and charge density. It is generally known that particles as small in size as the membrane pore are responsible for significant flux decline in microfiltration. For coagulated samples, smaller flocs produced filter cakes of higher specific resistance resulting from higher compressibility of the flocs (Lee et al., 2003; Cho et al., 2006). Therefore, change of floc particle size during the feed pre-treatment processes was examined in this work for obtaining a better understanding of the US-coagulation process and its impact on MF flux performance.

The effects of US on floc size for the feeds with different turbidity were investigated. Figure 5-13 shows the size distribution of the flocs of alum and ACH with and without US pre-treatment. The mean diameter of flocs after various pre-treatments was calculated using Mastersizer X software (Table 5-3). Flocs below 4 μm were not detected, which indicates that the fine particles were effectively adsorbed and/or trapped in the aluminium flocs. For all feed turbidity conditions tested, ACH led to larger flocs than alum, with and without US pre-treatment. US led to increased floc sizes for both alum (by 25–30 μm) and ACH (by 20–25 μm). Therefore, the improved flux was related to the increased floc size after US treatment. Although the particle size for the US-alum treated effluent was almost the same as for the ACH treated effluent, the filtration performance of the former was higher. It should be noted that the filterability of coagulated water depends not only on the floc size but also on the structure of flocs as suggested by Lee et al. (2003), Cho at al. (2006) and Wang et al. (2008). The results suggest that the difference in filtration resistance was mainly due to the different physical structures of the cake layer as observed in the ESEM images.

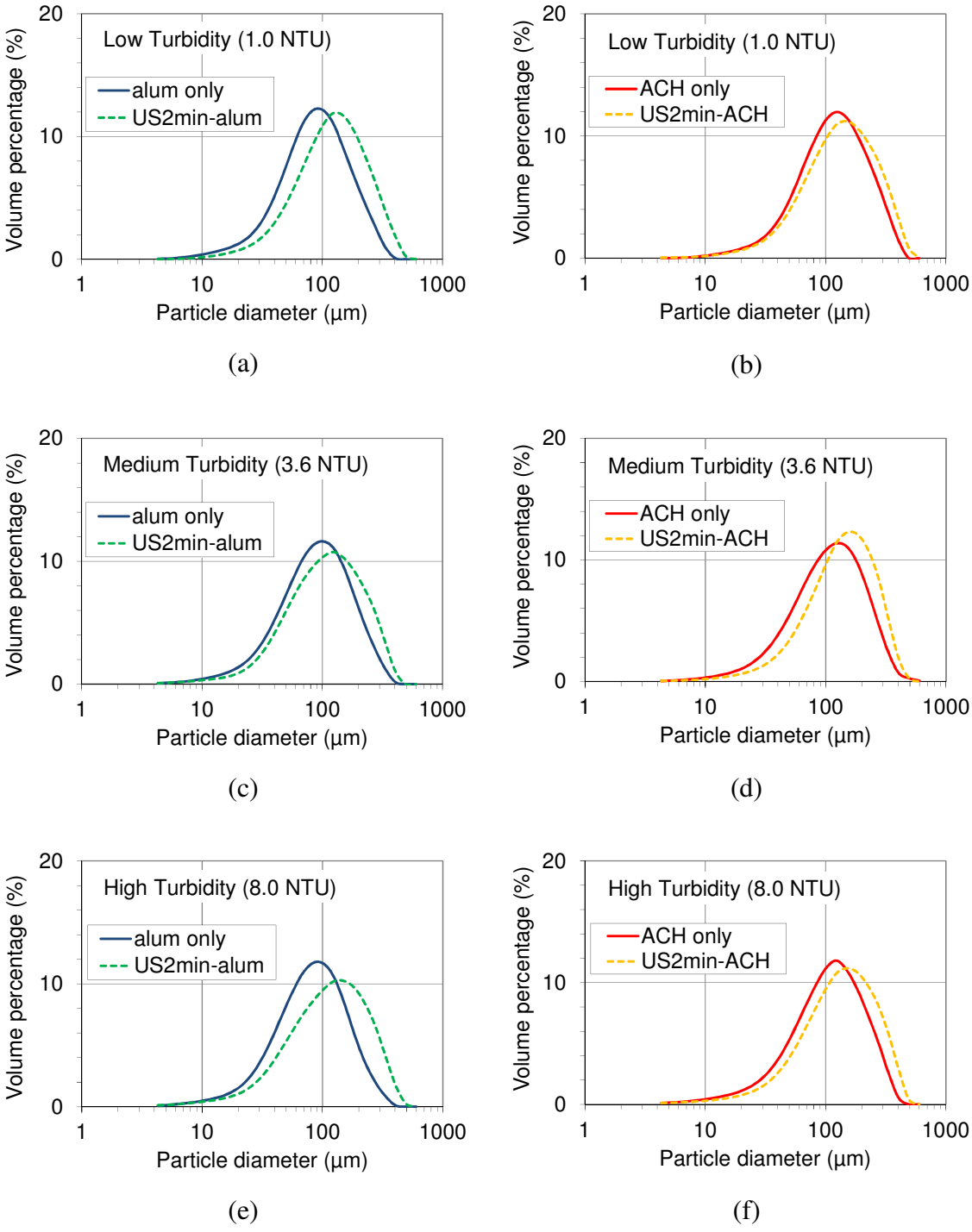


Figure 5-13 Size distribution of alum and ACH flocs with and without US pre-treatment at (a) and (b) low turbidity, (c) and (d) medium turbidity, (e) and (f) high turbidity

Table 5-3 Mean diameter (µm) of alum and ACH flocs with and without US pre-treatment

Sample	Alum only	US-alum	ACH only	US-ACH
Low turbidity (1.0 NTU)	93 ±5	123 ±6	122 ±9	142 ±9
Medium turbidity (3.6 NTU)	95 ±3	117 ±8	116 ±7	140 ±5
High turbidity (8.0 NTU)	94 ±0	123 ±15	116 ±7	140 ±5

5.6 *Cyclical cleaning tests*

Cyclical tests were conducted to investigate the change in reversibility of membrane fouling for coagulated effluent. The effluent used in this experiment which had relatively low turbidity and low SUVA (1.2 NTU, 1.6 L m^{-1} mg^{-1}) was collected on 09 March 2011, the same date as the sample used for cyclical US cleaning tests in section 4.3. Flux profiles of the effluent treated by ACH without and with sonication for 2 min before dosing the coagulant are illustrated in Figure 5-14a and Figure 5-14b, respectively. Figure 5-15a and Figure 5-15b show the permeate flux of coagulated effluent using alum without and with US pre-treatment, respectively.

The permeate flux decreased markedly with every cycle for ACH without sonication up to specific volume of 300 L m^{-2}, but when the effluent was exposed to US prior to coagulation the reduction was markedly reduced. US increased the permeate flux of the ACH treated effluent by approximately 38% at the end of cycle 5.

Although a reduction in the flux was experienced after the first backwashing for alum, the flux patterns overlapped after the second cycle. This shows that the affinity of alum-treated effluent for membranes reduced once the first alum layer was established on the membrane surface. The combination of US and alum pre-treatment improved the MF performance and the permeate flux could be restored by backwashing. This indicated

that the foulants of alum flocs were more easily removed from the membrane surface with hydraulic cleaning. The alum flocs, residual alum and organics which were not stabilised by the coagulation had a lower affinity for the membrane materials, compared with ACH. One of the reasons for lower filtration performance after ACH coagulation may be due to the structure of the flocs. As described in several reports, the polymeric aluminium species form tridecamers, Al_{13} (so-called Keggin structure), which are tighter and more stable than the hexameric rings formed by monomeric alum (Duan and Gregory, 2003; Wang et al., 2008; Parthasarathy and Buffle, 1985). The links between the flocs, and the flocs and the membrane may have increased during the cyclical operation due to compaction under the pressurised conditions.

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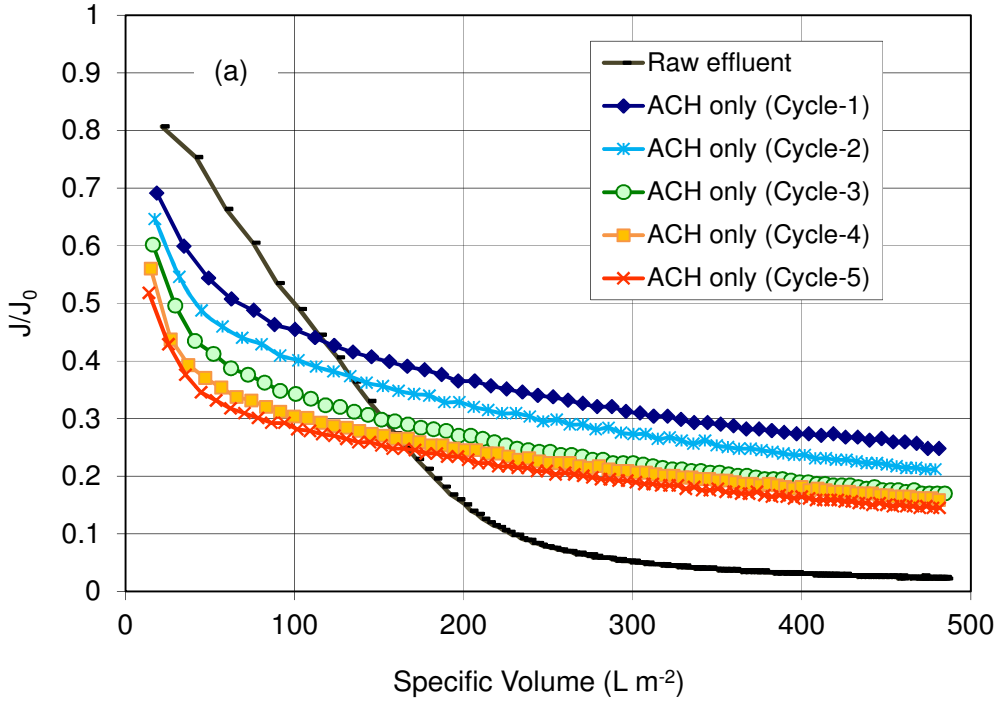


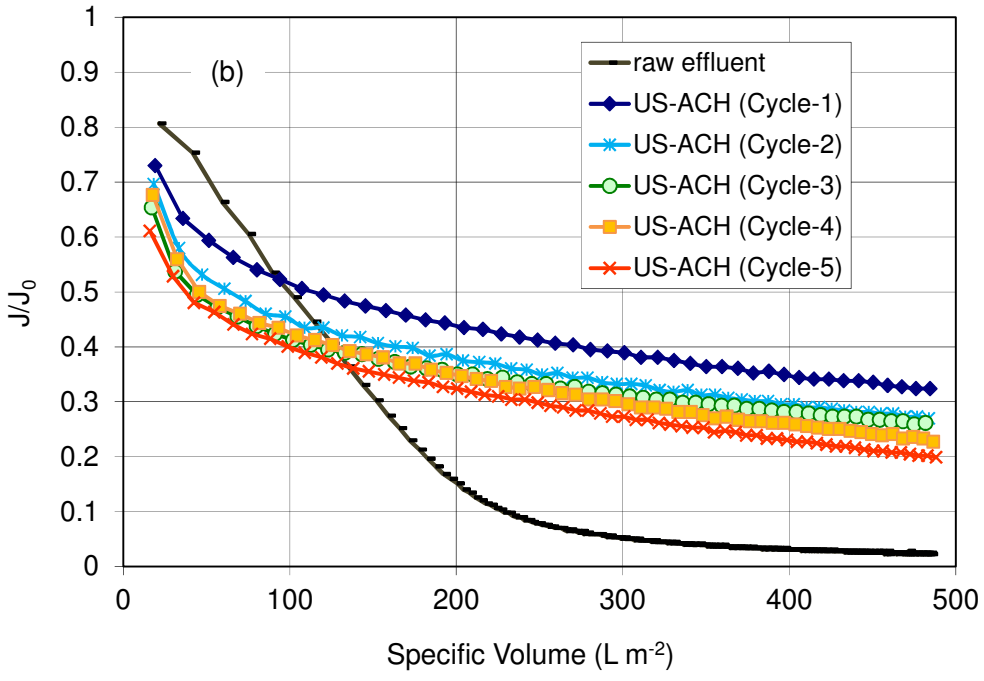
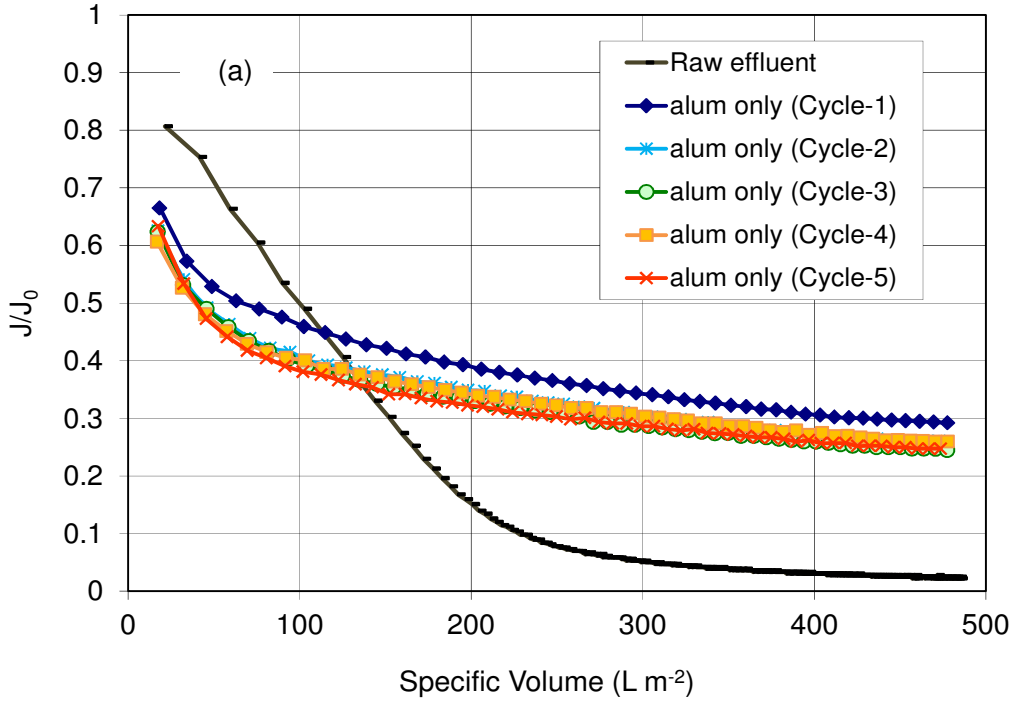


Figure 5-14 Permeate flux for MF of raw and effluent pre-treated by (a): ACH coagulation and (b): combination of US (2 min) and ACH coagulation



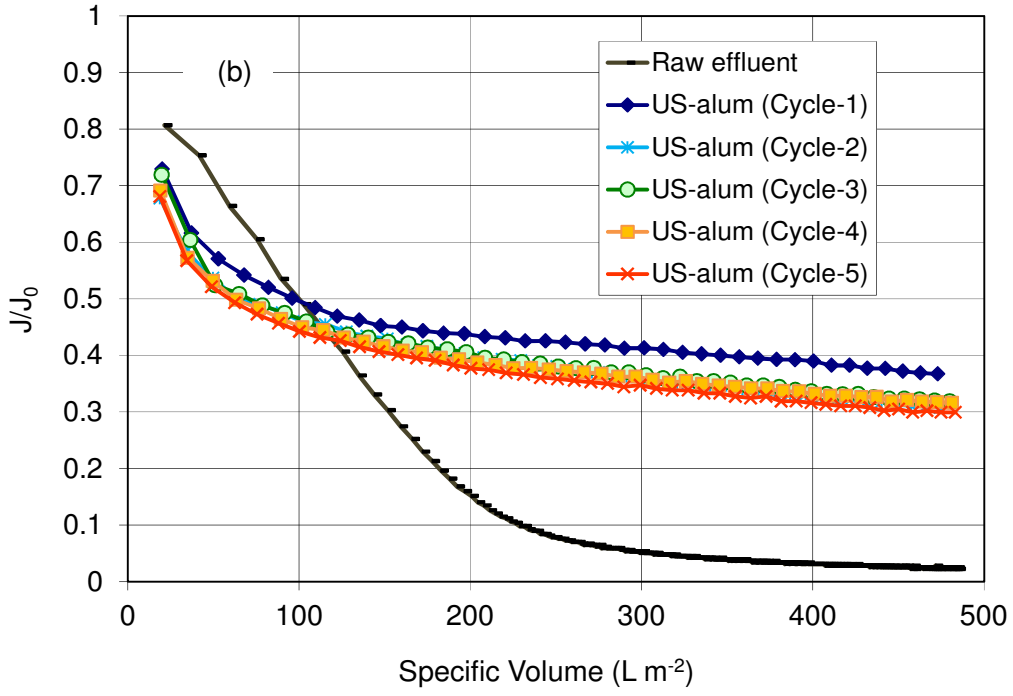


Figure 5-15 Permeate flux for MF of raw and effluent pre-treated by (a): alum coagulation and (b): combination of US (2 min) and alum coagulation

As shown in Figure 5-16, flux recovery for the raw effluent was much lower than for the coagulated effluent, and it decreased with successive cycles. In contrast, flux recovery for the coagulated effluent in the first cycle was very high (around 95%), although a little lower for ACH pre-treatment. However, after the second and subsequent cycles considerable and progressive reduction in the flux recovery was observed for the ACH coagulated samples. US pre-treatment followed by ACH coagulation gave higher flux recovery (by 3–5%) than feed without US pre-treatment in the 5 consecutive cycles. There was only a marginal difference in the flux recovery for the US duration of 2 and 5 min. For alum treatment, the initial flux could be almost completely restored by backwashing over the 5 cycles, such that the flux recovery was over 90%. Unlike ACH, US pre-treatment had little influence on the flux recovery of the membranes fouled with alum treated effluent, the flux recovery being slightly increased compared with alum treatment alone.

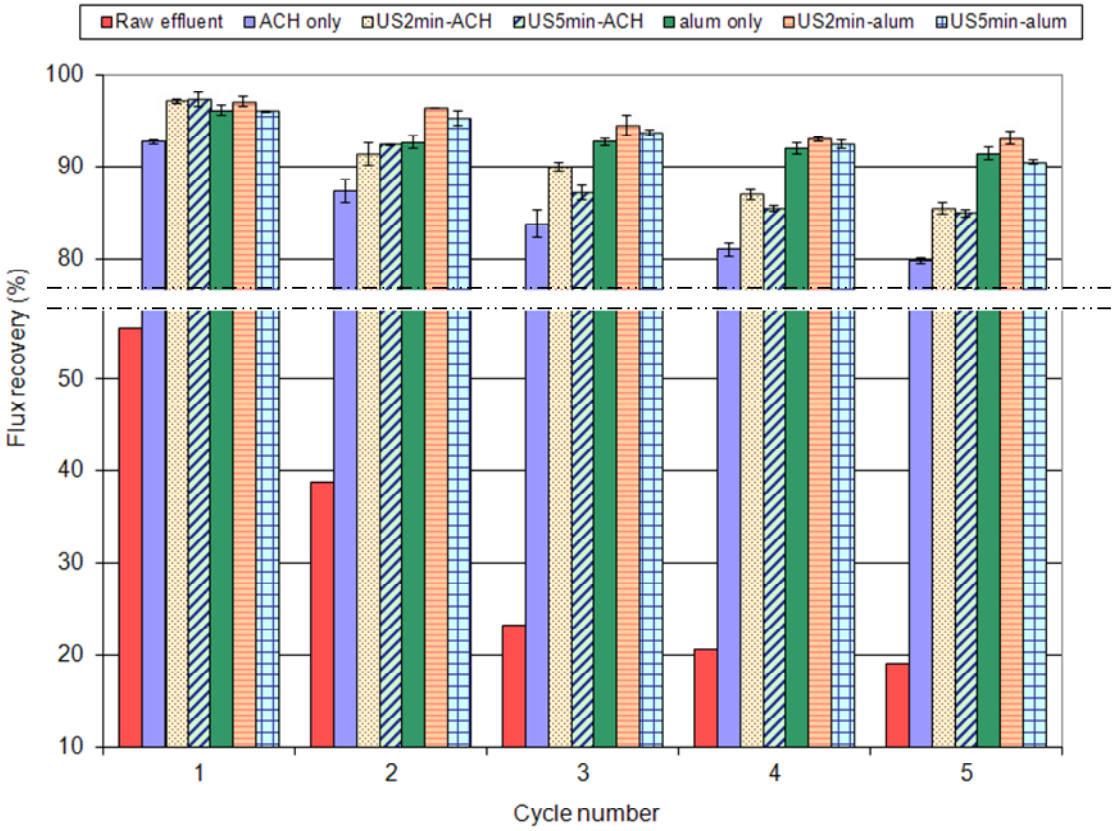
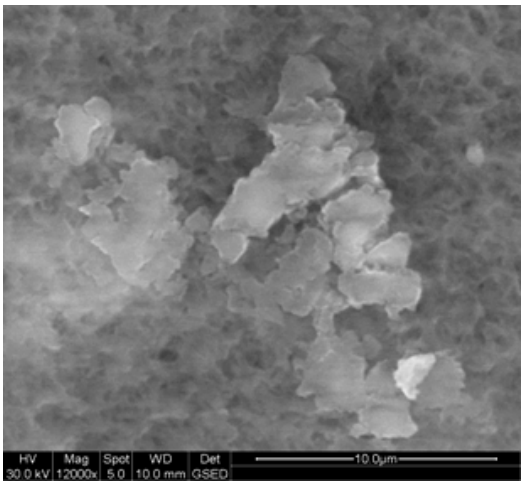


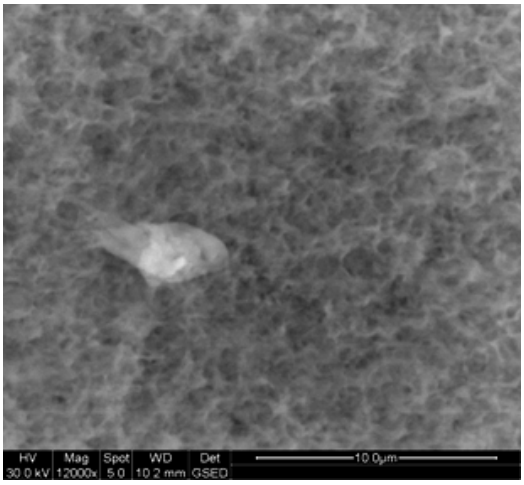
Figure 5-16 Flux recovery of membranes fouled with raw effluent, effluent pre-treated by Al^{3+}-based coagulation or combination of US and coagulation, after cyclical fouling and cleaning with backwashing

ESEM images and EDX spectra of the membrane surfaces after 5 fouling and cleaning cycles showed clear differences between ACH and alum (Figures 5-17 and 5-18). The results shown in these figures are representative of the foulants on their surfaces.

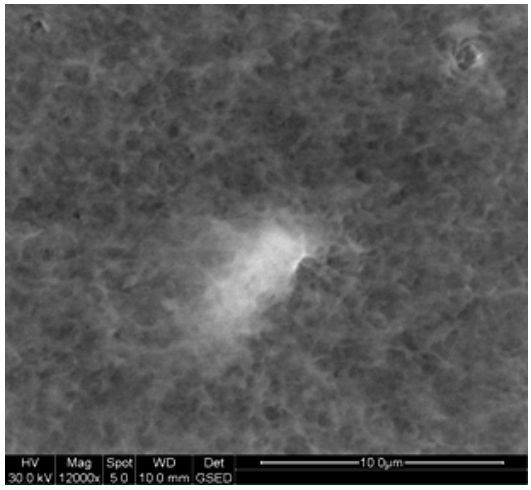


a. ACH only

b. US 2 min + ACH



c. alum only



d. US 2 min + alum

Figure 5-17 ESEM images (x 12000) of the surfaces of the cleaned membranes after 5 fouling and cleaning cycles (bar represents 10 µm)

For ACH significant patches of foulants remained on the membrane surface (Figure 5-17a). The corresponding EDX spectrum (Figure 5-18a) showed a large peak for aluminium and a minor peak for phosphorus (the latter attributed to precipitation of phosphate from the effluent by the Al), carbon, fluorine and oxygen which make up the membrane, and the carbon and oxygen also being due to the EfOM; this demonstrated

that ACH flocs adhered to the membrane. For US-ACH treated effluent there were some small particles remaining on the surface of the membrane (Figure 5-17b) but not as much as for ACH alone. The elemental components on the surface were carbon, oxygen and fluorine, indicative of the membrane and traces of EfOM, but not of ACH coagulum as no Al was detected (Figure 5-18b). The surfaces of the membranes for alum alone and US-alum treatment showed the membrane structure and only a few traces of deposit (Figures 5-17c and 5-17d). No aluminium was detected on the membrane surface for either alum or US-alum (Figure 5-18c and 5-18d), which proved that the alum flocs were readily removed by hydraulic cleaning.

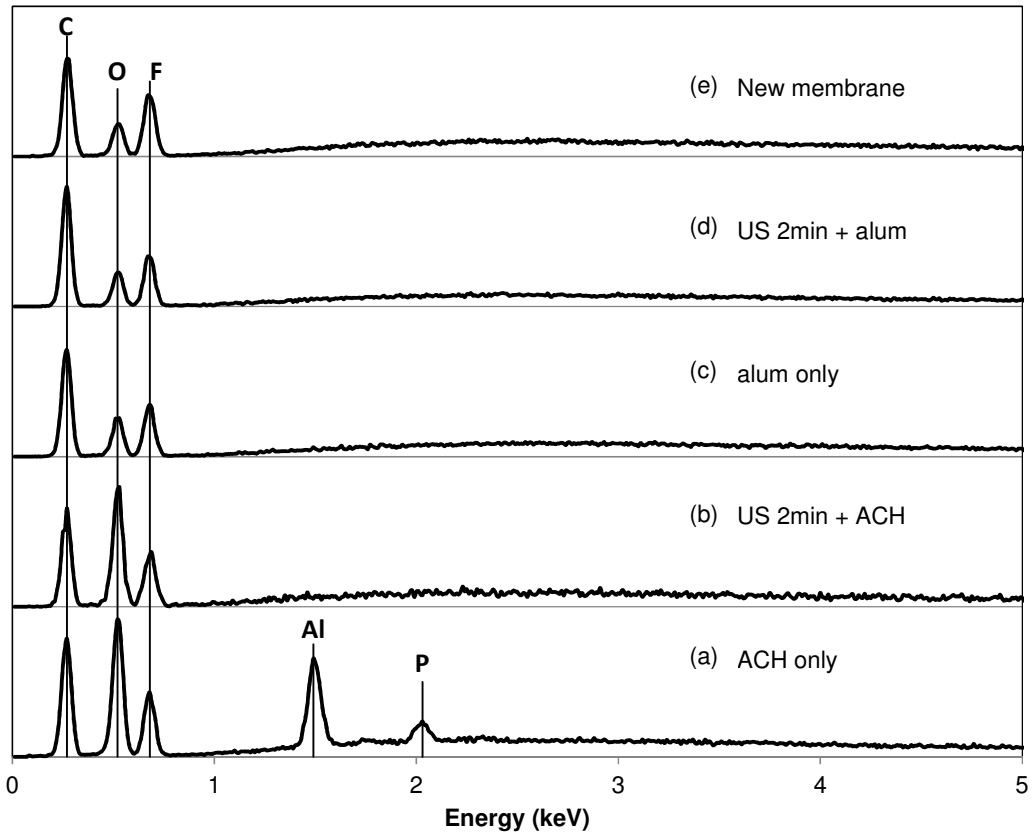


Figure 5-18 EDX spectra of the surfaces of the cleaned membranes after 5 cycles of cleaning

ATR-FTIR spectra for the organic substances remaining on the membranes after 5 fouling and cleaning cycles are shown in Appendix B. The ATR-FTIR spectra demonstrated that alum pre-treatment was superior with regard to membrane cleaning as

there were no organic substances left on the membrane surfaces, whereas weak peaks for polysaccharides and proteins were observed for ACH.

The adsorption characteristics of the alum and ACH flocs to the membrane material were slightly different. The affinity between the membrane and ACH flocs and the ACH flocs themselves was greater than for alum flocs, which was apparent in the ESEM and EDX results. The different levels of organic removal (i.e., reduction in DOC and UV absorbance and biopolymers shown in section 5.4.2) observed for ACH and alum indicates that the types of residual matter which were not adsorbed or trapped in the flocs could have also influenced the cleaning performance. US can make the affinity weaker by modifying the surface properties of EfOM and forming a cake layer which compacts less. The cake layer of alum flocs was generally less compacted and more easily removed by backwashing, therefore there was no marked reduction in irreversible fouling observed for US-alum. Moreover, the characteristics of the organic solutes may have been altered by adding alum, which reduced their potential to adsorb to membrane pore walls, as suggested by Kim (2005). This can be explained by the slightly higher DOC value of the permeate for the effluent coagulated by alum, compared with ACH.

5.7 *Summary of findings for US feed pre-treatment*

The effect of US feed pre-treatment on membrane performance in the MF of a biologically treated municipal effluent was investigated. Although there was a more rapid reduction in MF permeate flux with increasing duration of US pre-treatment, there was a marked reduction in irreversible fouling. US treatment of the effluent fragmented the suspended solids, consequently the resultant smaller particles accelerated the clogging of the membrane pores. It was demonstrated that US could structurally alter some of the highly fouling organic components such as biopolymers, resulting in less interaction of the effluent organics with the membranes and hence reducing hydraulically irreversible fouling. However, prolonged US feed pre-treatment may counteract the reduction of irreversible fouling.

Using US prior to Al^{3+}-based coagulation gave a marked increase in permeate flux. This was attributed to change in physico-chemical properties of the effluent organic matter leading to enhanced coagulation resulting in the formation of a cake layer having lower filtration resistance. The floc layer formed by ultrasonically treated then coagulated effluent appeared to be more porous than for the effluent without sonication (Figure 5-7). Furthermore, floc size increased significantly after US pre-treatment, resulting in a mean diameter 20–30 μm larger. The effect of US on decreased cake layer resistance was turbidity dependent for both alum and ACH, which indicates that the interaction of particulates and colloids with Al species may have played important roles in the morphology of coagulation flocs. On the other hand, the removal of dissolved organic compounds by coagulation and MF was not affected by US pre-treatment.

Irreversible fouling for MF was significantly decreased after coagulation pre-treatment with flux recovery of > 90% and > 80%, respectively, for alum and ACH, over the 5 cycle cleaning test. US pre-treatment markedly enhanced the mitigating effect of ACH on irreversible fouling, whereas since alum coagulation gave consistently high flux recovery, the improvement due to sequential US and alum pre-treatment was marginal. This was shown to be due to the alum flocs, and by inference, the remaining dissolved organics, having lower affinity for the membranes, hence the further effect of US on improving flux recovery was marginal.

Chapter 6. Conclusions and recommendations

6.1 *Conclusions*

The effectiveness of ultrasound (US) for the cleaning of membranes fouled with an activated sludge-lagoon effluent was demonstrated in this lab-scale study. US for 5–15 min gave a better flux recovery than backwashing (80–85 % cf. 75%). For US cleaning alone, the maximum cleaning effect was achieved after 10 min irradiation. When US was followed by backwashing the cleaning efficiency was enhanced. Analyses of the fouled membrane confirmed that the recalcitrant components in the effluent organic matter causing hydraulically irreversible fouling were protein-like and polysaccharide-like materials which were derived from the biological process. US was effective for dislodging the foulants on the membrane surface and very likely for loosening the foulants blocking the pores. Consequently, the loosened foulants were easily transported away from the membrane pores which led to the improvement in flux recovery. Although US produced a marked improvement in detachment of the fouling, some internal fouling of the membrane remained.

Cyclical cleaning of the membranes fouled with the raw effluent showed that the reduction in flux recovery was greater for backwashing than for US. After five cleaning cycles, the flux recovery for US was 64%, which was three times the flux recovery for backwashing, and the decline in the permeate flux was less than 10% (cf. 50% for backwashing). Surface analysis of membranes after US cleaning using ATR-FTIR suggested that US did not have any significant impact on membrane integrity after the 5 cycles. Although no damage was observed and the quality of product water was consistent in this short term experiment, the effects over many hundreds of cycles should be investigated as US can degrade polymers.

Despite its negative impact on the permeate flux, US pre-treatment resulted in a marked improvement in flux recovery. This can be explained as an increase in the number of smaller particles, resulting from destruction of the suspended solids by US, accelerating the pore plugging and hence causing a marked decrease in permeate flux. It was shown

that biopolymers, which are considered to have a high fouling potential, were structurally modified by US and so had reduced affinity with the membrane and/or other effluent organics. However, the effect may be offset by exposing the effluent to prolonged sonication resulting in increased adsorption on the pore walls.

US feed pre-treatment followed by Al^{3+}-based coagulation enhanced MF performance compared with coagulation alone. This was attributed to the reduced filtration resistance of the fouling layer which resulted from the enhanced coagulation due to the US induced modification of the effluent organics and breakdown of the particulates which aided nucleation. The cake layer formed by the US-coagulation treated effluent was more porous than that for coagulation only. This was in accordance with the observation that the floc size increased by approximately 20 and 30% for ACH and alum, respectively, after the US feed pre-treatment. The effect of US on the MF performance appeared to be turbidity dependent, with water with higher turbidity giving greater improvement compared with lower turbidity.

In cyclical cleaning, ACH-alone treated effluent caused greater irreversible fouling than alum. When US was employed prior to ACH, the affinity of the flocs and dissolved organic substances for the membrane may be reduced which was shown by the surface investigation using ESEM, EDX and ATR-FTIR. Consequently, flux recovery showed a significant increase over the multi-cycle cleaning. This effect was marginal for alum coagulation which itself led to high flux recovery.

US shows the potential to be used as an effective pre-treatment to alum coagulation of biologically treated effluent for enhancing MF permeate flux, particularly for the feed with higher turbidity. It is recommended to use alum, rather than ACH, as higher flux recovery was achieved due to alum flocs being more readily removed from the membrane. Concerning operating costs, it was reported that a typical energy consumption of MF for water reclamation is 0.4 kWh m^{-3} at an operating pressure range of 70-100 kPa (Asano, 2007), which is equivalent to A\$0.04 m^{-3}. Pre-treatment with alum requires A\$0.017 m^{-3} for the chemical cost at a dose of 5 mg L^{-1} as Al (i.e., an alum dose of 62 g m^{-3}) (unit cost of alum: A\$0.27 kg^{-1}, Shu et al., 2006). Although the costs associated with sludge handling will be inevitable, the use of alum would be cost-

effective as it increases the permeate flux about 4.5 times and reduces irreversible fouling significantly. The energy consumption of the US feed pre-treatment in this study was 1.84 kWh per m^3 effluent, which appeared to be high. However, the combination of US and alum coagulation enhanced average permeate flux 5.8 fold in single-cycle runs and gave nearly full flux recovery after hydraulic cleaning. The effect of US-alum pre-treatment on mitigating irreversible fouling was more significant in cyclical filtration tests. Thus, the use of US prior to coagulation can reduce the frequency of hydraulic and chemical cleaning, which would result in increased productivity and decreased maintenance costs for membrane water treatment systems. However, the process needs to be optimised for minimal energy input and maximum process cost effectiveness.

6.2 *Recommendations*

US coupled with chemical cleaning may have a greater effect on removing internal fouling. It was reported in several publications that US boosted the effectiveness of chemicals and so could reduce chemical consumption. However, there has been little such research conducted for municipal wastewater reclamation, further work may therefore be needed to investigate the efficacy of this membrane cleaning regime.

In this lab-scale study, an ultrasonic bath was employed for membrane cleaning, which is not very practical for actual filtration processes. In situ application of both US and backwashing would be better in practice. However, a major challenge may be the installation of ultrasound transducers in the filtration apparatus to enable uniform application of US to the membranes. Some researchers developed filtration cells with embedded US transducers and most of the US cleaning setups were only available for small flat sheet membranes, as presented by Lamminen et al. (2006). One of the options may be the application for cleaning submerged membranes due to their simple configuration.

For US pre-treatment, the apparent changes in EfOM characteristics in this study were the reduction in particle size and the destruction of peptide bonds. More detailed investigation of the US-induced changes of EfOM, such as surface charge and contact angle, is necessary for obtaining a better understanding of the mechanisms involved in

the mitigation of irreversible fouling. The use of protein solutions or fractionated EfOM may allow the identification of the influence of specific fractions.

Coagulation using charge neutralisation may show different behaviour in membrane filtration due to the mechanism involving charge interactions with EfOM. Compared with sweep flocculation, the floc formation mainly occurs via interaction of negatively charged EfOM and positively charged Al species. Therefore functionally altered EfOM may undergo greater or less interaction with Al and so supply us with better understanding of the mechanism.

It is generally known that the effects of low frequency US are mainly due to the mechanical forces of cavitation and acoustic streaming. However, it is not clear whether the modification is primarily attributable to physical (i.e., shear force) or sonochemical effects (i.e., reaction caused by radical species and H_2O_2). High frequency US in the range 100–300 kHz has been reported to induce the production of a higher amount of hydrogen peroxide (Nasseri et al., 2006). Optimisation of the operating parameters under different conditions would help to determine this and allow trade-off between reduced fouling and reduce power consumption.

References

Al-Amoudi, A. and Lovitt, R. W. (2007). Fouling strategies and the cleaning system of NF membranes and factors affecting cleaning efficiency. *Journal of Membrane Science,* 303**,** 4-28.

Amy, G. (2008). Fundamental understanding of organic matter fouling of membranes. *Desalination,* 231**,** 44-51.

APHA (1998). *Standard Methods for the Examination of Water and Wastewater, 20th edn,* Washington, DC, American Public Health Association, American Water Works Association, Water Environment Federation.

Asano, T. (2007). *Water reuse: issues, technologies, and applications*, McGraw-Hill.

Ashokkumar, M., Lee, J., Zisu, B., Bhaskarcharya, R., Palmer, M. and Kentish, S. (2009). Hot topic: Sonication increases the heat stability of whey proteins. *Journal of Dairy Science,* 92**,** 5353-5356.

Bachmann, M. A., Gordon, W. L., Koenig, J. L. and Lando, J. B. (1979). An infrared study of phase-III poly(vinylidene fluoride). *Journal of Applied Physics,* 50**,** 6106-6112.

Bae, T.-H. and Tak, T.-M. (2005). Effect of TiO_2 nanoparticles on fouling mitigation of ultrafiltration membranes for activated sludge filtration. *Journal of Membrane Science,* 249**,** 1-8.

Bai, R. and Leow, H. F. (2002). Microfiltration of activated sludge wastewater--the effect of system operation parameters. *Separation and Purification Technology,* 29**,** 189-198.

Baroña, G. N. B., Cha, B. J. and Jung, B. (2007). Negatively charged poly(vinylidene fluoride) microfiltration membranes by sulfonation. *Journal of Membrane Science,* 290**,** 46-54.

Benz, M. and Euler, W. B. (2003). Determination of the crystalline phases of poly(vinylidene fluoride) under different preparation conditions using differential scanning calorimetry and infrared spectroscopy. *Journal of Applied Polymer Science,* 89**,** 1093-1100.

Boccaccio, T., Bottino, A., Capannelli, G. and Piaggio, P. (2002). Characterization of PVDF membranes by vibrational spectroscopy. *Journal of Membrane Science,* 210**,** 315-329.

Bottero, J. Y., Axelos, M., Tchoubar, D., Cases, J. M., Fripiat, J. J. and Fiessinger, F. (1987). Mechanism of formation of aluminum trihydroxide from keggin Al13 polymers. *Journal of Colloid and Interface Science,* 117**,** 47-57.

Brant, J. A., Kwan, P., Daniel, U. and Valencia, R. (2010). Pilot-scale evaluation of chemical cleaning protocols for organic and biologically fouled microfiltration membranes *Journal of Environmental Engineering,* 136**,** 542-553.

Bratby, J. (2006). *Coagulation and Flocculation in Water and Wastewater Treatment*, IWA Publishing.

Cai, M., Wang, S., Zheng, Y. and Liang, H. (2009). Effects of ultrasound on ultrafiltration of *Radix astragalus* extract and cleaning of fouled membrane. *Separation and Purification Technology,* 68**,** 351-356.

Carroll, T., King, S., Gray, S. R., Bolto, B. A. and Booker, N. A. (2000). The fouling of microfiltration membranes by NOM after coagulation treatment. *Water Research,* 34**,** 2861-2868.

Chakraborti, R. K., Atkinson, J. F. and Van Benschoten, J. E. (2000). Characterization of alum floc by image analysis. *Environmental Science & Technology,* 34**,** 3969-3976.

Chang, I.-S., Le Clech, P., Jefferson, B. and Judd, S. (2002). Membrane fouling in membrane bioreactors for wastewater treatment. *Journal of Environmental Engineering,* 128.

Chapman, H., Vigneswaran, S., Ngo, H. H., Dyer, S. and Aim, R. B. (2002). Pre-flocculation of secondary treated wastewater in enhancing the performance of microfiltration. *Desalination,* 146**,** 367-372.

Chen, D., Weavers, L. K., Walker, H. W. and Lenhart, J. J. (2006). Ultrasonic control of ceramic membrane fouling caused by natural organic matter and silica particles. *Journal of Membrane Science,* 276**,** 135-144.

Chen, W., Westerhoff, P., Leenheer, J. A. and Booksh, K. (2003). Fluorescence excitation−emission matrix regional integration to quantify spectra for dissolved organic matter. *Environmental Science & Technology,* 37**,** 5701-5710.

Chen, Y., Dong, B. Z., Gao, N. Y. and Fan, J. C. (2007). Effect of coagulation pretreatment on fouling of an ultrafiltration membrane. *Desalination,* 204**,** 181-188.

Cheng, W. P. (2002). Comparison of hydrolysis/coagulation behavior of polymeric and monomeric iron coagulants in humic acid solution. *Chemosphere,* 47**,** 963-969.

Cho, M.-H., Lee, C.-H. and Lee, S. (2006). Effect of flocculation conditions on membrane permeability in coagulation-microfiltration. *Desalination,* 191**,** 386-396.

Choi, K. Y.-j. and Dempsey, B. A. (2004). In-line coagulation with low-pressure membrane filtration. *Water Research,* 38**,** 4271-4281.

Chow, C. W. K., van Leeuwen, J. A., Fabris, R. and Drikas, M. (2009). Optimised coagulation using aluminium sulfate for the removal of dissolved organic carbon. *Desalination,* 245**,** 120-134.

Crittenden, J., Trussell, R. R., Hand, D. W. and Howe, K. J. (2005). *Water Treatment: Principles and Design*, John Wiley & Sons, Inc.

Czechowska-Biskup, R., Rokita, B., Lotfy, S., Ulanski, P. and Rosiak, J. M. (2005). Degradation of chitosan and starch by 360-kHz ultrasound. *Carbohydrate Polymers,* 60**,** 175-184.

Donalson, J. C. (2009). *Adsorptive Fouling and Flux Decline of Microfiltration Membranes for Activated Sludge Basin Effluents.* Master of Science, University of Nevada.

Duan, J. and Gregory, J. (2003). Coagulation by hydrolysing metal salts. *Advances in Colloid and Interface Science,* 100-102**,** 475-502.

Fan, L., Nguyen, T., Roddick, F. A. and Harris, J. L. (2008). Low-pressure membrane filtration of secondary effluent in water reuse: Pre-treatment for fouling reduction. *Journal of Membrane Science,* 320**,** 135-142.

Farahbakhsh, K., Svrcek, C., Guest, R. K. and Smith, D. W. (2004). A review of the impact of chemical pretreatment on low-pressure water treatment membranes. *Journal of Environmental Engineering and Science,* 3**,** 237-253.

Feng, D., van Deventer, J. S. J. and Aldrich, C. (2006). Ultrasonic defouling of reverse osmosis membranes used to treat wastewater effluents. *Separation and Purification Technology,* 50**,** 318-323.

Flösch, D., Lehmann, H. D., Reichl, R., Inacker, O. and Göpel, W. (1992). Surface analysis of poly(vinylidene difluoride) membranes. *Journal of Membrane Science,* 70**,** 53-63.

Gander, M., Jefferson, B. and Judd, S. (2000). Aerobic MBRs for domestic wastewater treatment: a review with cost considerations. *Separation and Purification Technology,* 18**,** 119-130.

Goh, Y. T., Harris, J. L. and Roddick, F. (2010). Reducing the effect of cyanobacteria in the microfiltration of secondary effluent. *Water Science & Technology,* 62**,** 1682-1688.

Gregor, J. E., Nokes, C. J. and Fenton, E. (1997). Optimising natural organic matter removal from low turbidity waters by controlled pH adjustment of aluminium coagulation. *Water Research,* 31**,** 2949-2958.

Gregory, J. and Dupont, V. (2001). Properties of flocs produced by water treatment coagulants. *Water Science & Technology,* 44**,** 231-236.

Gülseren, I., Güzey, D., Bruce, B. D. and Weiss, J. (2007). Structural and functional changes in ultrasonicated bovine serum albumin solutions. *Ultrasonics Sonochemistry,* 14**,** 173-183.

Güzey, D., Gülseren, İ., Bruce, B. and Weiss, J. (2006). Interfacial properties and structural conformation of thermosonicated bovine serum albumin. *Food Hydrocolloids,* 20**,** 669-677.

Haberkamp, J., Ruhl, A. S., Ernst, M. and Jekel, M. (2007). Impact of coagulation and adsorption on DOC fractions of secondary effluent and resulting fouling behaviour in ultrafiltration. *Water Research,* 41**,** 3794-3802.

Henze, M. (2002). *Wastewater Treatment: Biological and Chemical Processes*, Springer.

Henze, M. (2008). *Biological wastewater treatment: principles, modelling and design*, IWA Pub.

Hong, S. and Elimelech, M. (1997). Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. *Journal of Membrane Science,* 132**,** 159-181.

Howe, K. J. and Clark, M. M. (2006). Effect of coagulation pretreatment : on membrane filtration performance. *American Water Works Association,* 98**,** 133-146.

Howe, K. J., Marwah, A., Chiu, K.-P. and Adham, S. S. (2006). Effect of coagulation on the size of MF and UF membrane foulants. *Environmental Science & Technology,* 40**,** 7908-7913.

Huang, H., Schwab, K. and Jacangelo, J. G. (2009). Pretreatment for low pressure membranes in water treatment: A review. *Environmental Science & Technology,* 43**,** 3011-3019.

Jambrak, A. R., Mason, T. J., Lelas, V., Herceg, Z. and Herceg, I. L. (2008). Effect of ultrasound treatment on solubility and foaming properties of whey protein suspensions. *Journal of Food Engineering,* 86**,** 281-287.

Jarusutthirak, C. (2002). *Fouling and Flux Decline of Reverse Osmosis (RO), Nanofiltration (NF), and Ultrafiltration (UF) Membranes Associated with Effluent*

Organic Matter (EfOM) during Wastewater Reclamation/Reuse. Ph.D. Thesis, University of Colorado at Boulder.

Jarusutthirak, C. and Amy, G. (2006). Role of soluble microbial products (SMP) in membrane fouling and flux decline. *Environmental Science & Technology,* 40**,** 969-974.

Jarusutthirak, C., Amy, G. and Croué, J.-P. (2002). Fouling characteristics of wastewater effluent organic matter (EfOM) isolates on NF and UF membranes. *Desalination,* 145**,** 247-255.

Jiang, J.-Q. (2001). Development of coagulation theory and pre-polymerized coagulants for water treatment. *Separation & Purification Reviews,* 30**,** 127-141.

Jung, B. (2004). Preparation of hydrophilic polyacrylonitrile blend membranes for ultrafiltration. *Journal of Membrane Science,* 229**,** 129-136.

Kang, S.-K. and Choo, K.-H. (2006). Use of submerged microfiltration membranes for glass industry wastewater reclamation: pilot-scale testing and membrane cleaning. *Desalination,* 189**,** 170-180.

Kim, S.-H., Moon, S.-Y., Yoon, C.-H., Yim, S.-K. and Cho, J.-W. (2005). Role of coagulation in membrane filtration of wastewater for reuse. *Desalination,* 173**,** 301-307.

Kimura, K., Maeda, T., Yamamura, H. and Watanabe, Y. (2008). Irreversible membrane fouling in microfiltration membranes filtering coagulated surface water. *Journal of Membrane Science,* 320**,** 356-362.

Kobayashi, M., Tashiro, K. and Tadokoro, H. (1975). Molecular vibrations of three crystal forms of poly(vinylidene fluoride). *Macromolecules,* 8**,** 158-171.

Kobayashi, T., Chai, X. and Fujii, N. (1999). Ultrasound enhanced cross-flow membrane filtration. *Separation and Purification Technology,* 17**,** 31-40.

Kobayashi, T., Kobayashi, T., Hosaka, Y. and Fujii, N. (2003). Ultrasound-enhanced membrane-cleaning processes applied water treatments: influence of sonic frequency on filtration treatments. *Ultrasonics,* 41**,** 185-190.

Kyllönen, H. M., Pirkonen, P. and Nyström, M. (2005). Membrane filtration enhanced by ultrasound: a review. *Desalination,* 181**,** 319-335.

Laabs, C. N., Amy, G. L. and Jekel, M. (2006). Understanding the size and character of fouling-causing substances from effluent organic matter (EfOM) in low-pressure membrane filtration. *Environmental Science & Technology,* 40**,** 4495-4499.

Lamminen, M. O., Walker, H. W. and Weavers, L. K. (2004). Mechanisms and factors influencing the ultrasonic cleaning of particle-fouled ceramic membranes. *Journal of Membrane Science,* 237**,** 213-223.

Lamminen, M. O., Walker, H. W. and Weavers, L. K. (2006). Cleaning of particle-fouled membranes during cross-flow filtration using an embedded ultrasonic transducer system. *Journal of Membrane Science,* 283**,** 225-232.

Laurent, J., Casellas, M., Pons, M. N. and Dagot, C. (2009). Flocs surface functionality assessment of sonicated activated sludge in relation with physico-chemical properties. *Ultrasonics Sonochemistry,* 16**,** 488-494.

Le-Clech, P., Chen, V. and Fane, T. A. G. (2006). Fouling in membrane bioreactors used in wastewater treatment. *Journal of Membrane Science,* 284**,** 17-53.

Lee, J.-D., Lee, S.-H., Jo, M.-H., Park, P.-K., Lee, C.-H. and Kwak, J.-W. (2000). Effect of coagulation conditions on membrane filtration characteristics in coagulation−microfiltration process for water treatment. *Environmental Science & Technology,* 34**,** 3780-3788.

Lee, N., Amy, G., Croué, J.-P. and Buisson, H. (2004). Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM). *Water Research,* 38**,** 4511-4523.

Lee, S. A., Fane, A. G., Amal, R. and Waite, T. D. (2003). The effect of floc size and structure on specific cake resistance and compressibility in dead-end microfiltration. *Separation Science and Technology,* 38**,** 869 - 887.

Leighton, T. G. (1997). *The Acoustic Bubble,* San Siego, Academic Press.

Li, Q., Xu, Z. and Pinnau, I. (2007). Fouling of reverse osmosis membranes by biopolymers in wastewater secondary effluent: Role of membrane surface properties and initial permeate flux. *Journal of Membrane Science,* 290**,** 173-181.

Li, T., Zhu, Z., Wang, D., Yao, C. and Tang, H. (2006). Characterization of floc size, strength and structure under various coagulation mechanisms. *Powder Technology,* 168**,** 104-110.

Lim, A. L. and Bai, R. (2003). Membrane fouling and cleaning in microfiltration of activated sludge wastewater. *Journal of Membrane Science,* 216**,** 279-290.

Mahamuni, N. N. and Adewuyi, Y. G. (2010). Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: A review with emphasis on cost estimation. *Ultrasonics Sonochemistry,* 17**,** 990-1003.

Mason, T. J. (1997). Ultrasound in synthetic organic chemistry. *Chemical Society Reviews,* 26**,** 443-451.

Mason, T. J., Lorimer, J. P. and Bates, D. M. (1992). Quantifying sonochemistry: Casting some light on a 'black art'. *Ultrasonics,* 30**,** 40-42.

Masselin, I., Chasseray, X., Durand-Bourlier, L., Lainé, J.-M., Syzaret, P.-Y. and Lemordant, D. (2001). Effect of sonication on polymeric membranes. *Journal of Membrane Science,* 181**,** 213-220.

Matilainen, A., Vepsäläinen, M. and Sillanpää, M. (2010). Natural organic matter removal by coagulation during drinking water treatment: A review. *Advances in Colloid and Interface Science,* 159**,** 189-197.

Melbourne Water (2011). *Western treatment plant*. http://education.melbournewater.com.au/content/sewage_and_recycling/western_treatment_plant/western_treatment_plant.asp [Accessed 10th july 2011].

Meng, F., Chae, S.-R., Drews, A., Kraume, M., Shin, H.-S. and Yang, F. (2009). Recent advances in membrane bioreactors (MBRs): Membrane fouling and membrane material. *Water Research,* 43**,** 1489-1512.

Meng, F., Zhang, H., Yang, F., Zhang, S., Li, Y. and Zhang, X. (2006). Identification of activated sludge properties affecting membrane fouling in submerged membrane bioreactors. *Separation and Purification Technology,* 51**,** 95-103.

Millipore (2011). *Durapore membrane filter, product family information*. http://www.millipore.com/catalogue/item/VVLP04700 [Accessed 10th July 2011].

Muthukumaran, S., Kentish, S. E., Stevens, G. W., Ashokkumar, M. and Mawson, R. (2007). The application of ultrasound to dairy ultrafiltration: The influence of operating conditions. *Journal of Food Engineering,* 81**,** 364-373.

Muthukumaran, S., Yang, K., Seuren, A., Kentish, S., Ashokkumar, M., Stevens, G. W. and Grieser, F. (2004). The use of ultrasonic cleaning for ultrafiltration membranes in the dairy industry. *Separation and Purification Technology,* 39**,** 99-107.

Naddeo, V., Belgiorno, V. and Napoli, R. M. A. (2007). Behaviour of natural organic mater during ultrasonic irradiation. *Desalination,* 210**,** 175-182.

Naddeo, V., Meriç, S., Kassinos, D., Belgiorno, V. and Guida, M. (2009). Fate of pharmaceuticals in contaminated urban wastewater effluent under ultrasonic irradiation. *Water Research,* 43**,** 4019-4027.

Naffrechoux, E., Chanoux, S., Petrier, C. and Suptil, J. (2000). Sonochemical and photochemical oxidation of organic matter. *Ultrasonics Sonochemistry,* 7**,** 255-259.

Nasseri, S., Vaezi, F., Mahvi, A. H., Nabizadeh, R. and Haddadi, S. (2006). Determination of the ultrasonic effectiveness in advanced wastewater treatment. *Iranian Journal of Environmental Health Science & Engineering,* 3**,** 109-116.

Nguyen, T., Fan, L., Roddick, F. A. and Harris, J. L. (2009). A comparative study of microfiltration and ultrafiltration of activated sludge-lagoon effluent. *Desalination,* 236**,** 208-215.

Parthasarathy, N. and Buffle, J. (1985). Study of polymeric aluminium(III) hydroxide solutions for application in waste water treatment. Properties of the polymer and optimal conditions of preparation. *Water Research,* 19**,** 25-36.

Pescod, M. B. (1992). Wastewater treatment and use in agriculture. *FAO irrigation and drainage paper* [Online], 47.

Pétrier, C. and Francony, A. (1997). Ultrasonic waste-water treatment: incidence of ultrasonic frequency on the rate of phenol and carbon tetrachloride degradation. *Ultrasonics Sonochemistry,* 4**,** 295-300.

Pétrier, C., Lamy, M.-F., Francony, A., Benahcene, A., David, B., Renaudin, V. and Gondrexon, N. (1994). Sonochemical Degradation of Phenol in Dilute Aqueous Solutions: Comparison of the Reaction Rates at 20 and 487 kHz. *The Journal of Physical Chemistry,* 98**,** 10514-10520.

Popovic, S., Djuric, M., Milanovic, S., Tekic, M. N. and Lukic, N. (2010). Application of an ultrasound field in chemical cleaning of ceramic tubular membrane fouled with whey proteins. *Journal of Food Engineering,* 101**,** 296-302.

Puspitasari, V., Granville, A., Le-Clech, P. and Chen, V. (2010). Cleaning and ageing effect of sodium hypochlorite on polyvinylidene fluoride (PVDF) membrane. *Separation and Purification Technology,* 72**,** 301-308.

Riesz, P. and Kondo, T. (1992). Free radical formation induced by ultrasound and its biological implications. *Free Radical Biology and Medicine,* 13**,** 247-270.

Salimi, A. and Yousefi, A. A. (2003). Analysis Method: FTIR studies of β-phase crystal formation in stretched PVDF films. *Polymer Testing,* 22**,** 699-704.

Shon, H. K., Vigneswaran, S. and Snyder, S. A. (2006). Effluent organic matter (EfOM) in wastewater: Constituents, effects, and treatment. *Critical Reviews in Environmental Science and Technology,* 36**,** 327-374.

Shu, L., Schneider, P., Jegatheesan, V. and Johnson, J. (2006). An economic evaluation of phosphorus recovery as struvite from digester supernatant. *Bioresource Technology,* 97**,** 2211-2216.

Singh, N., Husson, S. M., Zdyrko, B. and Luzinov, I. (2005). Surface modification of microporous PVDF membranes by ATRP. *Journal of Membrane Science,* 262**,** 81-90.

Sivakumar, M. and Pandit, A. B. (2001). Ultrasound enhanced degradation of Rhodamine B: optimization with power density. *Ultrasonics Sonochemistry,* 8**,** 233-240.

Song, L. (1998). Flux decline in crossflow microfiltration and ultrafiltration: mechanisms and modeling of membrane fouling. *Journal of Membrane Science,* 139**,** 183-200.

Stathopulos, P. B., Scholz, G. A., Hwang, Y.-M., Rumfeldt, J. A. O., Lepock, J. R. and Meiering, E. M. (2004). Sonication of proteins causes formation of aggregates that resemble amyloid. *Protein Science,* 13**,** 3017-3027.

Stork, D. (2008). *An Investigation into Membrane Fouling from Algae-containing Waters.* Master of Applied Science, RMIT University.

Sui, P., Wen, X. and Huang, X. (2008). Feasibility of employing ultrasound for on-line membrane fouling control in an anaerobic membrane bioreactor. *Desalination,* 219**,** 203-213.

Sumitomo electric fine polymer (2011). *Poreflon™ Membrane*. http://www.sei-sfp.co.jp/products/popup/list_08.html [Accessed 13th Aug 2011].

Susanto, H., Arafat, H., Janssen, E. M. L. and Ulbricht, M. (2008). Ultrafiltration of polysaccharide–protein mixtures: Elucidation of fouling mechanisms and fouling control by membrane surface modification. *Separation and Purification Technology,* 63**,** 558-565.

Suslick, K. S. (1989). The chemical effects of ultrasound. *Scientific American* 260**,** 80-86.

Szu, S. C., Zon, G., Schneerson, R. and Robbins, J. B. (1986). Ultrasonic irradiation of bacterial polysaccharides. Characterization of the depolymerized products and some applications of the process. *Carbohydrate Research,* 152**,** 7-20.

Thompson, P. L. and Paulson, W. L. (1998). Dewaterability of alum and ferric coagulation sludges. *Journal of American Water Works Association,* 90**,** 164-170.

Tiehm, A., Nickel, K., Zellhorn, M. and Neis, U. (2001). Ultrasonic waste activated sludge disintegration for improving anaerobic stabilization. *Water Research,* 35**,** 2003-2009.

Tran, T., Gray, S., Bolto, B., Farmer, T. D. and Collings, T. F. (2007). Ultrasound enhancement of microfiltration performance for natural organic matter removal. *Organic Geochemistry,* 38**,** 1091-1096.

Wang, J., Guan, J., Santiwong, S. R. and Waite, T. D. (2008). Characterization of floc size and structure under different monomer and polymer coagulants on microfiltration membrane fouling. *Journal of Membrane Science,* 321**,** 132-138.

Wang, J., Guan, J., Santiwong, S. R. and Waite, T. D. (2010). Effect of aggregate characteristics under different coagulation mechanisms on microfiltration membrane fouling. *Desalination,* 258**,** 19-27.

Water Environment Federation (2005). *Membrane Systems for Wastewater Treatment,* Alexandria, McGraw-Hill Professional.

Wilf, M. and Alt, S. (2000). Application of low fouling RO membrane elements for reclamation of municipal wastewater. *Desalination,* 132**,** 11-19.

Yan, M., Wang, D., Ni, J., Qu, J., Chow, C. W. K. and Liu, H. (2008). Mechanism of natural organic matter removal by polyaluminum chloride: Effect of coagulant particle size and hydrolysis kinetics. *Water Research,* 42**,** 3361-3370.

Yang, B., Jiang, Y., Zhao, M., Shi, J. and Wang, L. (2008). Effects of ultrasonic extraction on the physical and chemical properties of polysaccharides from longan fruit pericarp. *Polymer Degradation and Stability,* 93**,** 268-272.

Zhang, G., Ji, S., Gao, X. and Liu, Z. (2008). Adsorptive fouling of extracellular polymeric substances with polymeric ultrafiltration membranes. *Journal of Membrane Science,* 309**,** 28-35.

Zhu, H., Wen, X. and Huang, X. (2010). Membrane organic fouling and the effect of pre-ozonation in microfiltration of secondary effluent organic matter. *Journal of Membrane Science,* 352**,** 213-221.

Appendices

Appendix A EEM spectra of the raw effluent and coagulated effluent with and without ultrasonication

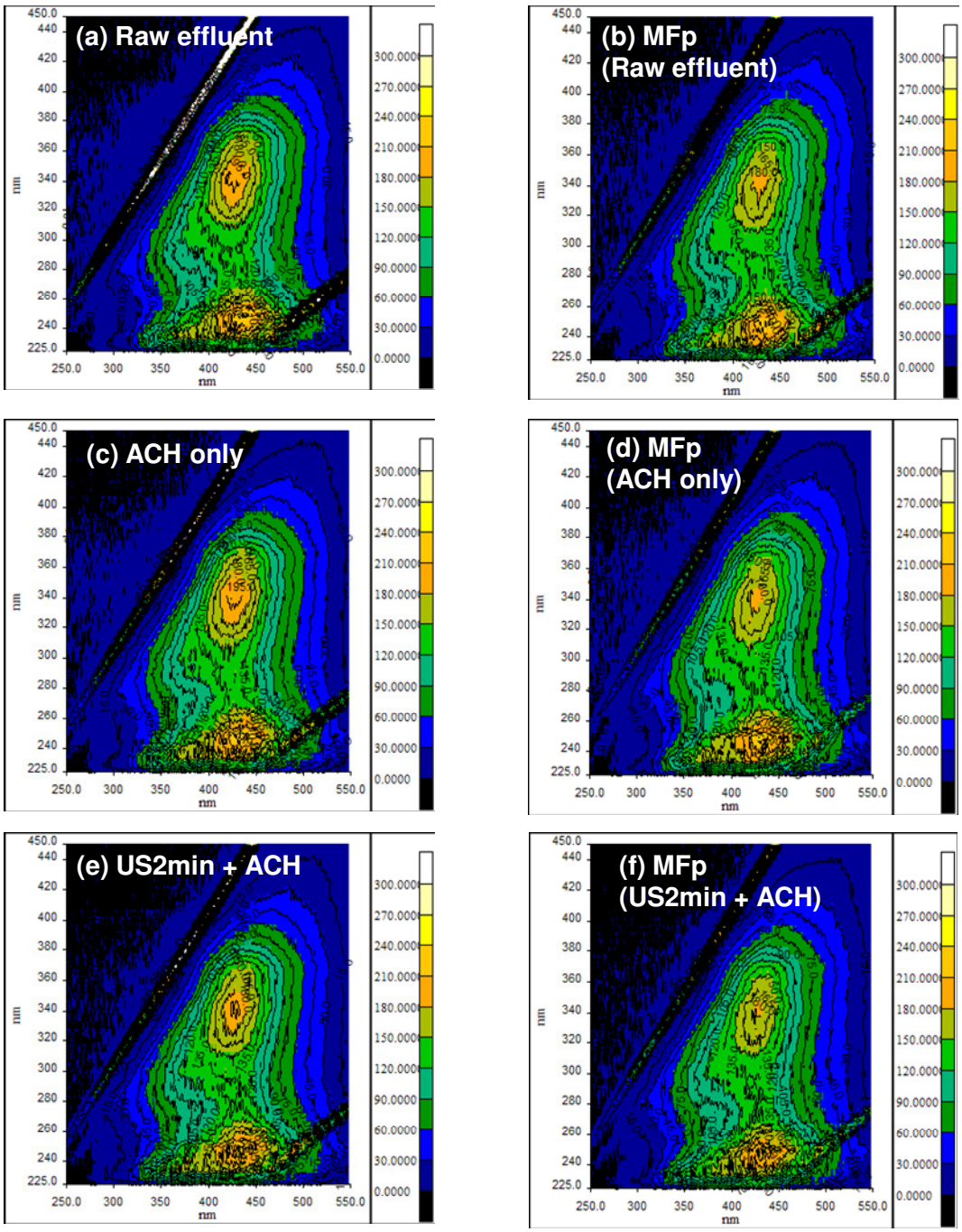


Figure 0-1 EEMs of the (a) raw effluent and effluent pre-treated with (c) ACH, (e) US for 2 min followed by ACH, and MF permeate of these (b), (d) and (f)

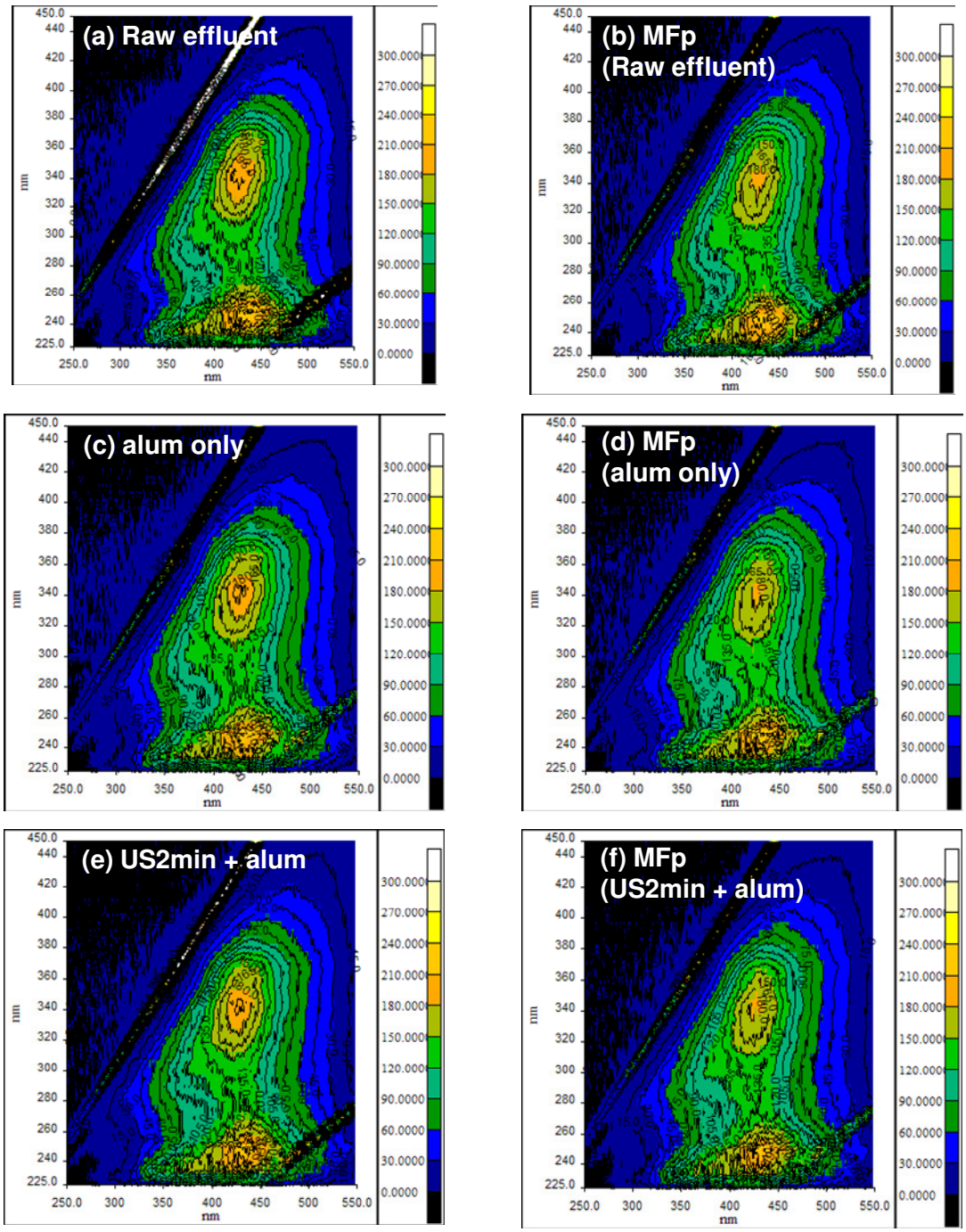


Figure 0-2 EEMs of the (a) raw effluent and effluent pre-treated with (c) alum, (e) US for 2 min followed by alum, and MF permeate of these (b), (d) and (f)

Appendix B ATR-FTIR spectra of new membrane and the membranes after 5 cycles of cleaning

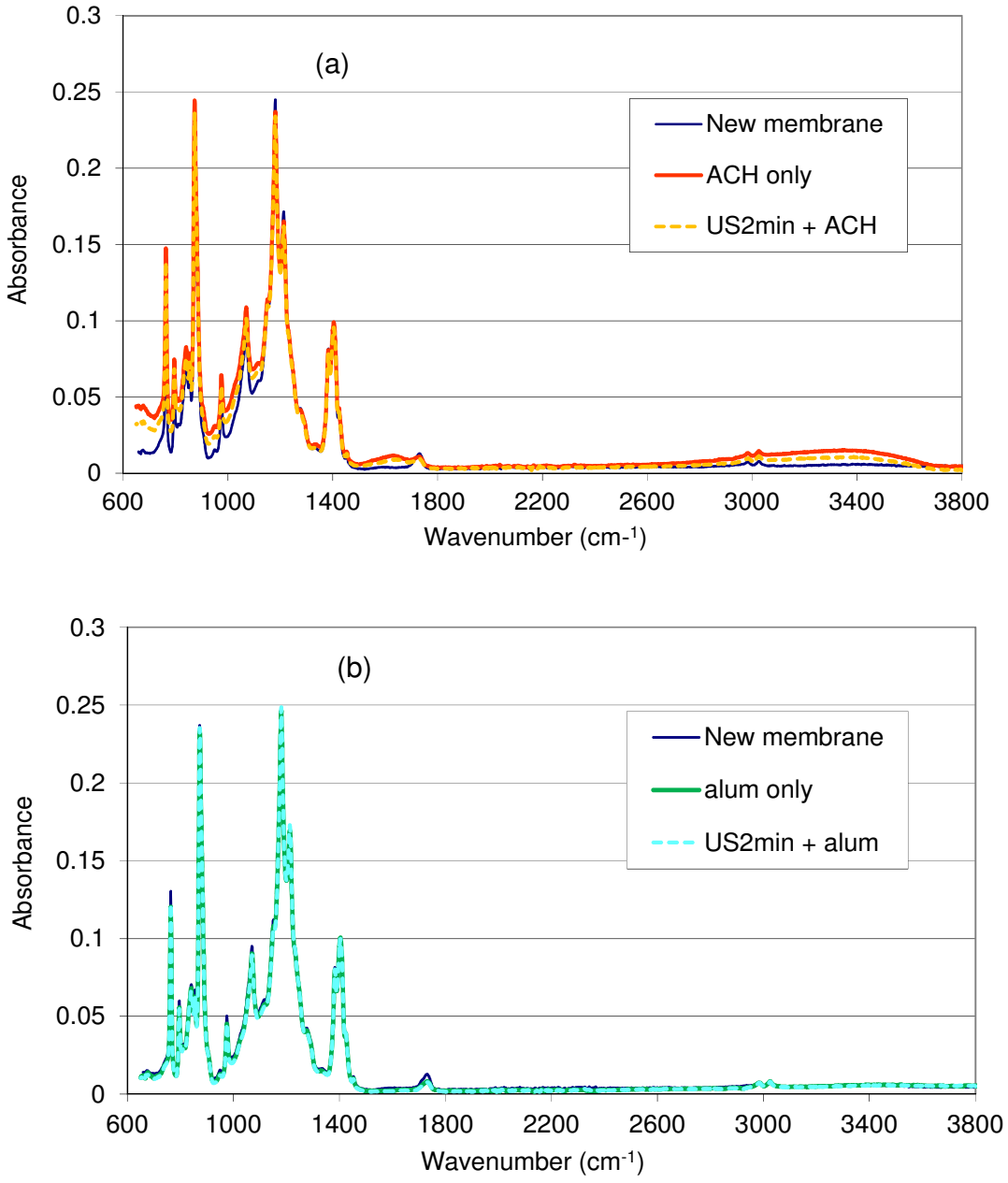


Figure 0-3 ATR-FTIR spectra of new membrane and the membranes after 5 cycles of cleaning. (a) the effluent pre-treated with ACH and a combination of US and ACH, (b) the effluent pre-treated with alum and a combination of US and alum